# DETERMINATION Of The ORIENTATION Of SUBSTITUENTS In NAPHTHALENE DERIVATIVES.

By

ROBERT R. H. BROWN, B.Sc.

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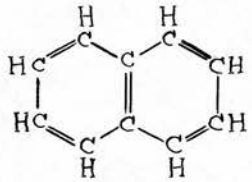
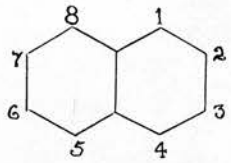
# I N T R O D U C T I O N.

Naphthalene was discovered in coal tar by Garden in 1819 (Annals of Phil., 1820, 15, 74). The symmetrical formula given below, which represents the molecule as composed of two six-membered rings having two carbon atoms in common, was assigned to it in 1866 by Erlenmeyer, and is known as the Erlenmeyer-Gräbe formula.



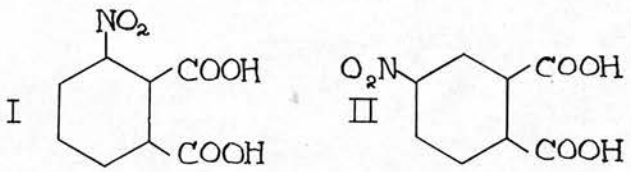
To indicate the orientation of substituents, several methods for distinguishing the positions have been devised, but that now generally in use is the one proposed by Gräbe in 1869, and adopted by the Geneva Congress on Nomenclature in 1892.



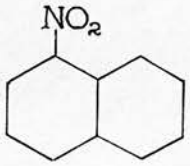

From the formula it will be seen that the mono-derivatives of naphthalene can exist in two series, according to whether or not the substituent is attached

to an atom adjacent to one of the carbon atoms common to both rings - that is, compounds obtained by replacement of one of the four equivalent hydrogen atoms 1, 4, 5 or 8 are known as α-compounds, and those obtained by substituting one of the four equivalent atoms 2, 3, 6 or 7 as β-compounds. A disubstitution product of naphthalene may occur in ten isomerides if the two substituents are similar, or in fourteen isomerides if they are different. With the entry of more than two atoms or groups into the molecule the number of isomerides is very much larger. It is on account of this large number of isomerides, and also the lack of methods for proving their constitution, that the chemistry of naphthalene derivatives has not been worked out so fully as that of benzene derivatives.

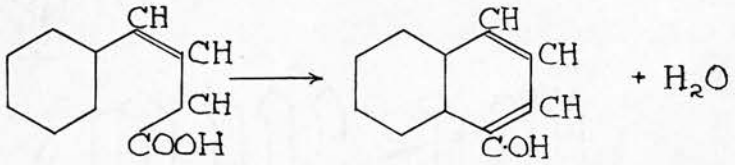
In the case of the mono-derivatives, oxidation to the corresponding phthalic acids can frequently be used to determine whether the atoms or groups are attached at the α- or β- positions. For example, Reverdin and Nötling (Ber., 1880, 13, 36; Bull. [2], 1880, 33, 107) prepared a mononitronaphthalene which on oxidation with chromic acid yielded a nitro-phthalic acid of melting point 218°, which must have either one or other of the formulae:-



These acids were both known and the one obtained was identified with I, so that the nitro-naphthalene was proved to be the α-derivative:-




Another method which has been applied to mono-derivatives is that of synthesis. For example, Fittig and Erdmann (Ber., 1883, 16, 43; Ann., 1885, 227, 242) found that α-naphthol was obtained from β-benzylidene-propionic acid (phenyl-isocrotonic acid) by heating:-




The genetic relations of other compounds with these, such as α-naphthylamine, α-naphthalene sulphonic acid, etc., decided their constitution, as well as indirectly differentiating them from the β-derivatives.

A remarkable property of the naphthalene molecules is the great tendency to form α-derivatives. Nevertheless, on sulphonation at high temperatures, β-naphthalene sulphonic acid is obtained, although the α-derivative is produced at lower temperatures. This phenomenon is, however, explained by the fact that the α-acid, when heated with sulphuric acid, passes over into the β-acid, so that apparently even

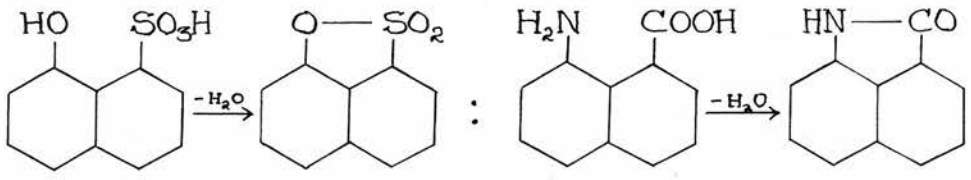
at higher temperatures the α-acid is formed first.

As previously stated the number of isomeric disubstituted naphthalene derivatives is large, so that they have not been studied as fully as the mono-derivatives. With many polysubstituted naphthalene compounds oxidation to the corresponding phthalic acid derivatives can also be used for the determination of the positions of the substituents. A second method is to convert the compound concerned into another naphthalene derivative of known constitution. This method has many applications among the disubstituted derivatives - in a number of cases the dichloro-naphthalenes have been employed as a standard of reference, since all the possible dichloro-compounds are known. Dichloronaphthalenes can be obtained by the action of phosphorus pentachloride on various disubstituted naphthalenes; examples of such compounds are those containing the following groups:- (1) the hydroxyl group, (2) the amino group which may be displaced via the diazo and hydroxyl groups, (3) sulphonic group through the intermediate sulphochloride, (4) nitro group.

The work of Armstrong and Wynne completely cleared up the question of the dichloronaphthalenes; they characterised the individual isomers by the preparation of their corresponding sulphochlorides. Twelve isomeric dichloronaphthalenes were formerly

reputed to exist, whereas the formula only predicts ten. In the course of this work, however, Armstrong and his co-workers proved that one of the reputed isomers was a mixture of two others, and another was really a trichloronaphthalene.

Many disubstituted derivatives of naphthalene can be recognised by analogy with the corresponding compounds of the benzene series, as giving reactions characteristic of a particular type. Thus, the ortho-diamino derivatives of naphthalene yield condensation products with aldehydes and 1 : 2 diketones, which are analogous with those obtained from the ortho-diamines of the benzene series; similarly, 1:4 aminonaphthol and 1:4-dihydroxynaphthalene on oxidation yield α-naphthoquinone and are therefore characterised as para-compounds. On the other hand, the 1:8 derivatives undergo typical reactions in forming ring complexes through the elimination of water, e.g.,




8-Naphthol-1-sulphonic Acid. Naphtho-sultone. 8-Amino-1-naphthoic Acid. Naphtha-styril.

These are known as peri-substituted compounds and have no analogues in the benzene series.

With higher substituted naphthalene

derivatives the number of isomers increases, and the difficulties of determining the positions of the substituents are accordingly greater. In this thesis two comparatively simple reactions have been used for converting certain polysubstituted naphthalene derivatives into known naphthalene compounds. The historical development of these reactions is traced in the sequence.

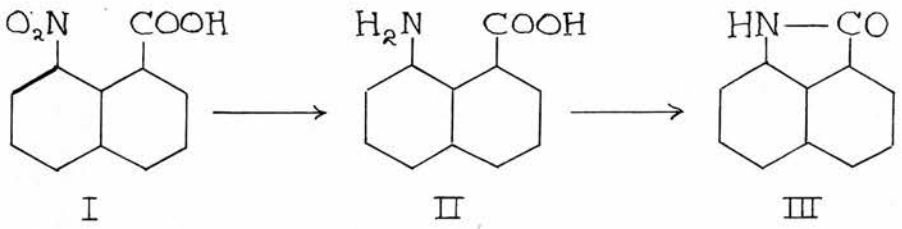
## Researches of Ekstrand on 1:8 Naphthalene Derivatives.

Since much of the important work bearing on derivatives of this type was carried out by Ekstrand and published in two long communications in 1888, it is proposed to give a general survey of the results obtained by him and also by other investigators in this field.

The first 8-halogenated naphthoic acid to be prepared was the 8-chloro-1-naphthoic acid (Ekstrand, J. pr., [2], 1888, 38, 139). As starting material potassium 1-naphthalene sulphonate was employed, from which by dry distillation with potassium ferrocyanide, 1-naphthonitrile was obtained (Witt, Ber., 1873, 6, 448).

This on subsequent hydrolysis gave 1-naphthoic acid.

By direct nitration of 1-naphthoic acid two mono-nitro acids were obtained which were separated by crystallisation from alcohol. The more soluble nitro-acid (I) was then reduced with alkaline ferrous sulphate to the corresponding amino-acid (II). By the ready formation of naphthastyril (III) from this compound, it was proved to have the 1:8 structure.



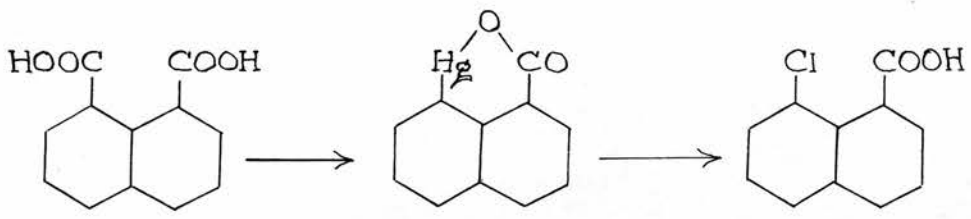

I II III

The 8-chloro-acid was prepared from this amino acid by Sandmeyer's method using a hot hydrochloric acid solution of cuprous chloride and the diazonium salt solution of the amino acid. Unfortunately, this method was long and tedious and only gave very small yields.

The 8-halogenated-1-naphthoic acids have recently been prepared in good yield from naphthastyril by Goldstein and Francey (Chim. Helv. Acta., 1932, XV, 1362). But naphthastyril is not a readily accessible compound so this method has its limitations. Naphthastyril was boiled with sodium hydroxide to form the sodium salt of the amino acid. The diazotisation

was effected by adding sodium nitrite and running the solution slowly into sulphuric acid, with cooling. The halogenated acids were prepared from the diazonium salt by means of the Sandmeyer reaction - treatment with cuprous chloride, cuprous bromide or potassium iodide yielded the chloro, bromo, and iodo acids respectively.

The best known method of preparing 8-bromo-1-naphthoic acid is that which has developed from the work of Whitmore and his co-workers on the mercuration of naphthalic acid. Naphthalic acid was first mercurated by boiling with mercuric acetate (Leuck, Perkins and Whitmore, J.A.C.S., 1929, 51, 1831). In order to prove the structure of the mercuration product it was subjected to chlorination (Whitmore and Fox, J.A.C.S., loc. cit., 3363). For this purpose it was dissolved in sodium hydroxide and the chloro-mercuric-derivative precipitated with hydrochloric acid. This compound was suspended in acetic acid and treated in the cold with a solution of chlorine in acetic acid, whereby 8-chloro-1-naphthoic acid was produced.




The bromo acid was readily prepared by treating the

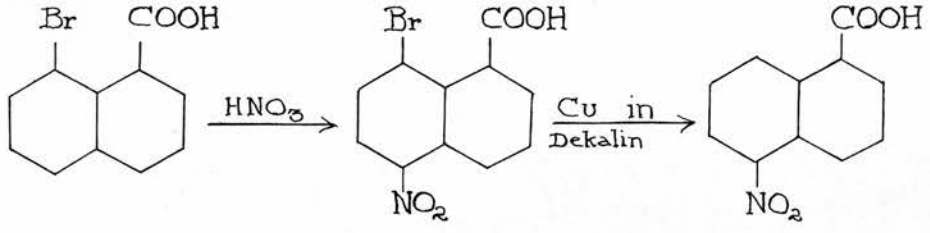
suspension of the chloromercuri-derivative with a solution of bromine in aqueous sodium bromide, but the iodo acid was not obtainable in this way.

This method for preparing 8-bromo-acids has been modified (Rule and Barnett, J.C.S., 1932, 175; Davies, Heilbron and Irving, J.C.S., 1932, 2715) so that 8-bromo-1-naphthoic acid is now readily obtainable in comparatively large quantity, thus opening the field for research on its further substitution.

The experimental section of this thesis is mainly concerned with derivatives of 8-bromo-1-naphthoic acid, their preparation and determination of their structure. The chief interest in the 8-halogenated-1-naphthoic acids is due to the great reactivity of the halogen atom in the peri-position. Rule and Barnett (J.C.S., 1932, 2728) from a recent investigation of the reactivities of ortho-iodo-benzoic acid and 8-bromo-1-naphthoic acid found that, in general, the halogen atom in the peri-position is more easily replaceable than that in an ortho-substituted benzoic acid; it was suggested that one of the factors leading to this result is the greater proximity of the groups in the peri- as compared with the ortho-positions.

W. Pursell, working in these laboratories (Thesis, Edinburgh 1933) nitrated the above 8-bromo-1-naphthoic acid obtaining a mono-nitro derivative, but experienced difficulty in determining the position

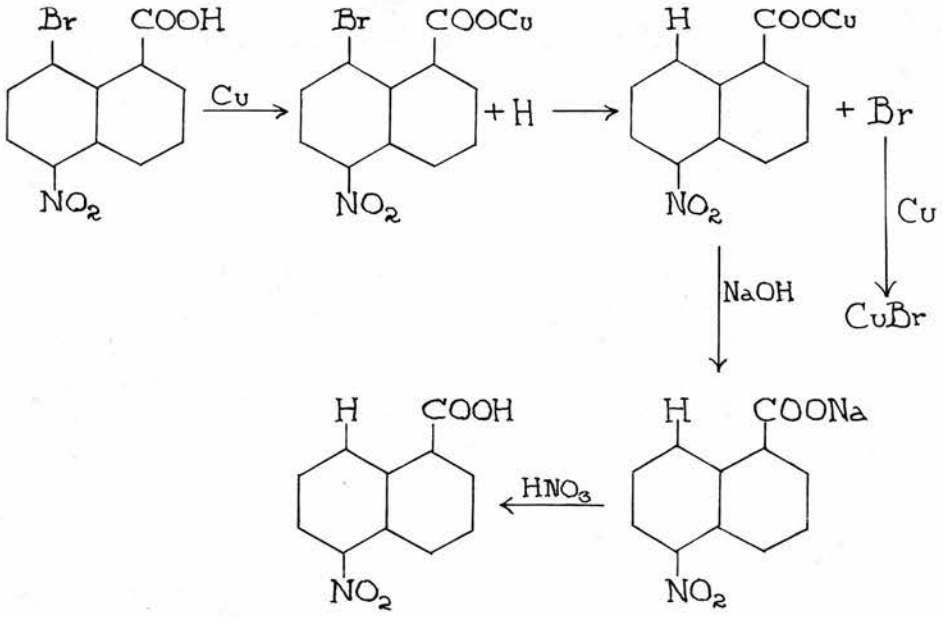
of the nitro group. It was found that the nitro-bromo-acid decomposed with the evolution of carbon dioxide when heated above its melting point, but the acid could not be converted into a nitro-bromo-naphthalene by this treatment. Reduction of the acid was then tried using ferrous sulphate and ammonia, metallic sodium, and hydriodic acid; however, in each case, although evidence was forthcoming that reduction had taken place, the product could not be purified. Eventually, however, dehalogenation was accomplished successfully by means of copper bronze. The nitro bromo acid was suspended in boiling dekalin and hydrogen bubbled through in presence of copper bronze for one hour. The resulting acid was taken up in alkali, the dekalin separated, and the acid re-precipitated with nitric acid. The product obtained, after recrystallisation, proved to be 5-nitro-1-naphthoic acid, thus proving the original acid to be 5-nitro-8-bromo-1-naphthoic acid.




This reaction was also applied with success to the mononitro-derivative of the 8-chloro-acid.

The method was somewhat modified in later experiments - toluene was used in place of dekalin,

and it was found that the hydrogen could be dispensed with, the hydrogen necessary for the reduction being obtained from the acid by the formation of the copper salt. Under the catalytic action of the copper, the hydrogen liberated replaces the bromine, which combines with the copper to form copper bromide. The sodium hydroxide used in the extraction decomposes the copper salt to give the sodium salt, from which the reduced acid is obtained by acidification. This is outlined in the following scheme:-



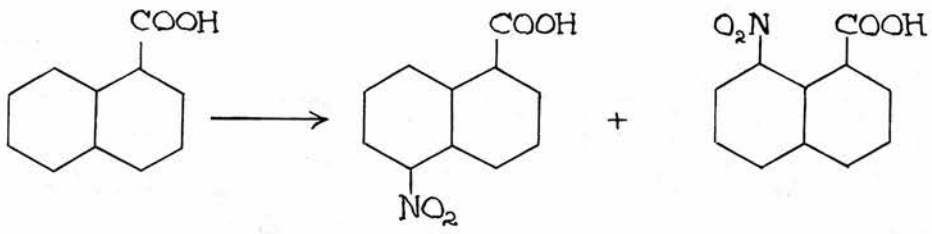

The validity of the above scheme was tested by three simple experiments:- (1) the ester could not be reduced by this means, there being no possibility of the formation of a copper salt to liberate hydrogen for the reduction; (2) the copper salt of the acid was prepared, but it could not be reduced by this method, there being no hydrogen liberated to effect the reduction; (3) if the copper functions only as a

catalyst the reaction should proceed in presence of only a trace of copper. It was found, however, that the reduction required copper in quantitative amount, so that the copper does not function solely as a catalyst. Thus it was proved that the reduction was brought about by the hydrogen from the carboxyl group, and it was concluded that the above mechanism is the probable one. Further confirmation was found in the fact that it was possible to supply hydrogen externally for the reduction of sodium-8-bromo-1-naphthoate and the corresponding ethyl ester.

It was observed that in the case of the halogenated benzoic acids only the ortho derivative can be reduced by this method, the meta and para isomers being unaffected. A similar effect was noted with the bromo-naphthoic acids. The 8-halogeno-compound and its nitro derivatives were easily reduced to the dehalogenated products, while the 5-bromo-1-naphthoic acid was quite unaffected. Thus, all the results appear to lead uniformly to the conclusion that the spatial position of the carboxyl group is a predominant factor in the reaction, since if the effects are transmitted through the bonds they would be expected to show at least to some degree in the cases of 5-bromo-1-naphthoic acid and meta and para-bromo-benzoic acids. A valuable feature of this reaction is that other groups or atoms present, such as the nitro group or

or halogen in other positions, are quite unaffected.

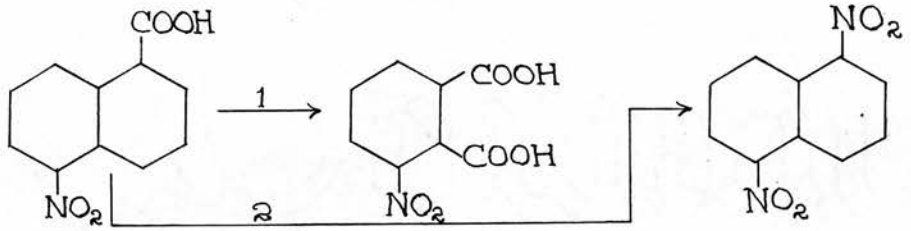
From a consideration of the work of Ekstrand (loc. cit.) it was to be expected that 8-bromo-1-naphthoic acid on nitration would yield 5-nitro-8-bromo-1-naphthoic acid. This author states in the summary of his work that from his experiments on the nitration and chlorination of α-naphthoic acid, it appears that the α-positions in the other benzene ring with respect to the carboxyl group, i.e. positions 5 and 8, are most readily substituted. Thus, he found that α-naphthoic acid on nitration yielded approximately equal amounts of the 5- and 8-nitro-acids:-




It is of interest to note the methods adopted by Ekstrand to establish the constitutions of these two acids.

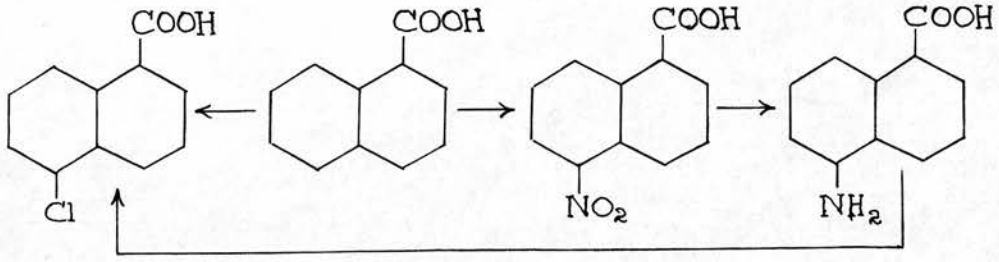
As previously stated (p. 7) he proved the structure of the 8-nitro acid by reducing it to the amino acid, from which naphthastyril was readily obtained by loss of water, thus proving the nitro group to be in the 8 position. The constitution of the 5-nitro acid was established thus:- (1) On oxidation with alkaline potassium permanganate or nitric acid (S.G. 1·12) the 5-nitro acid yielded

3-nitro-phthalic acid. (2) The 5-nitro acid was heated with excess nitric acid (S.G. 1·3). On cooling, it was treated with water, filtered, extracted with sodium carbonate and the alkali insoluble residue recrystallised from alcohol. The product proved to be 1:5-dinitronaphthalene. Hence the original acid was 5-nitro-1-naphthoic acid.



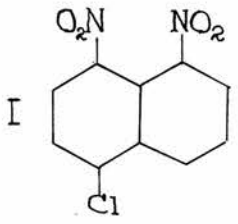

Ekstrand also obtained a dichloro-1-naphthoic acid by the direct chlorination of 8-chloro-1-naphthoic acid, but had to determine its constitution by indirect means. His argument is as follows.

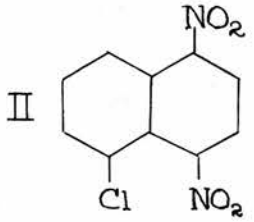
It was found that α-naphthoic acid on chlorination in acetic acid solution yielded a mono-chloro-acid. This proved to be the same as that obtained from 5-nitro-1-naphthoic acid by reduction, diazotisation, and replacing the diazo group with chlorine by means of the Sandmeyer reaction - thus proving it to be the 5-chloro-1-naphthoic acid.



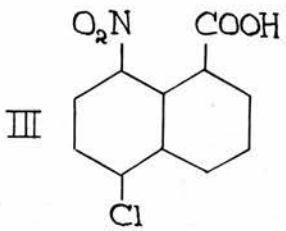
Ekstrand attempted to further chlorinate the 5-chloro acid to the dichloro compound but failed, although he obtained a higher chloro acid by indirect means. The 5-chloro acid was nitrated with fuming nitric acid, a mono-nitrochloro acid being obtained as well as a dinitrochloronaphthalene. This dinitrochloronaphthalene proved to be the same as that obtained by Atterberg (Ber., 1876, 9, 928), who also converted it into a trichloro-naphthalene (loc. cit., pp. 1733, 1735) in which the three chlorine atoms were proved to occupy α-positions.

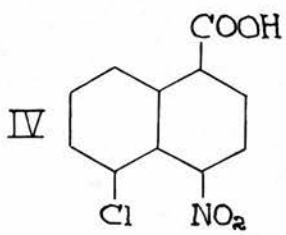
Since Ekstrand prepared this dinitro-chloronaphthalene from 5-chloro-1-naphthoic acid by nitration and replacement of the carboxyl group by a nitro group it must be formulated as either I or II.



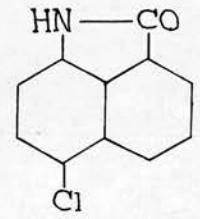




The mononitromonochloro-α-naphthoic acid must therefore have one or other of the formulae



This acid on reduction with ferrous sulphate and ammonia yielded an amino acid, which on warming with alcohol was completely converted into an anhydride - 5-chloro-naphthastyril:-

V 


The chloronitro acid was therefore formulated as 5-chloro-8-nitro-1-naphthoic acid, and the dinitro-chloronaphthalene as 1:8-dinitro-5-chloronaphthalene (formulae III and I above).

Similarly α-naphthoic acid on bromination in acetic acid solution yielded 5-bromo-1-naphthoic acid, which on nitration gave 5-bromo-8-nitro-1-naphthoic acid. The latter was converted on reduction into the amino acid and finally into 5-bromo-naphthastyril.

Ekstrand also diazotised 5-chloro-naphthastyril and replaced the diazo group by chlorine, thus obtaining a dichloro-α-naphthoic acid which must be 5:8-dichloro-1-naphthoic acid. This proved to be the same as that obtained by the direct chlorination of 8-chloro-1-naphthoic acid. In other words 8-chloro-1-naphthoic acid on chlorination yields 5:8-dichloro-1-naphthoic acid, a reaction which is analogous with the preparation by W. Pursell (Thesis, Edinburgh 1933) of

of 5-nitro-8-bromo-1-naphthoic acid by the direct nitration of 8-bromo-1-naphthoic acid.

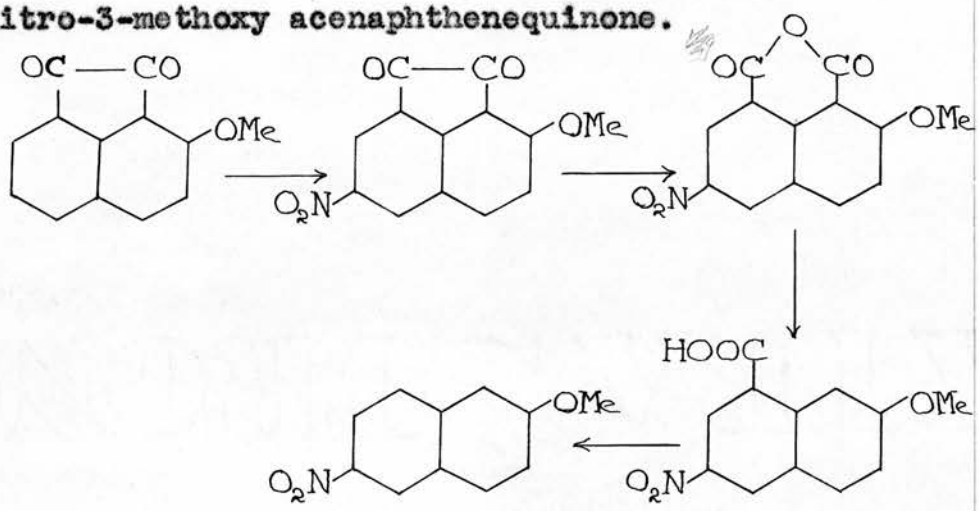
The foregoing 5-nitro-8-bromo-1-naphthoic acid was further nitrated by W. Pursell (loc. cit.) to give a dinitro-bromo-acid. All attempts, at this time, to orientate the position of the second nitro group failed, although the bromine atom in position 8 was successfully removed by the copper bronze method to give an unidentified dinitro-naphthoic acid. It was not found possible, however, to eliminate carbon dioxide from the latter by heating it above its melting point, and so to convert it into a known dinitro-naphthalene.

Within the last few years, however, a new technique has been developed for the decarboxylation of acids. Shepard, Winslow and Johnson (J.A.C.S., 1930, 52, 2083) observed that certain bromo- and chloro-furoic acids readily lost carbon dioxide on being heated to 210-300°, but that 3-chlorofuroic acid and 5-chlorofuroic acid were more stable and could not be decarboxylated in this way. They found, however, that copper bronze or finely-divided nickel effectively catalysed the decarboxylation and in presence of these catalysts 3-chlorofuroic acid and 5-chlorofuroic acid could be decarboxylated. It was thought that perhaps the pyrolysis of the halogenated furoic acids under the conditions employed might give rise through secondary

reactions to the formation of some free halogen acid, towards which the simpler furane derivatives are relatively sensitive. To avoid decomposition of the resulting halogenated furanes, the decarboxylation was therefore effected in presence of quinoline which would combine with any halogen acid liberated.

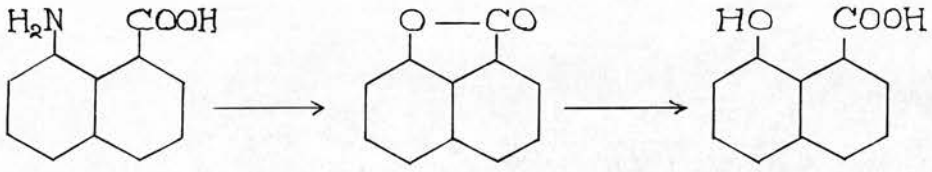
Davies, Heilbron and Irving (J.C.S., 1932, 2715) applied this reaction to the decarboxylation of substituted α-naphthoic acids. They nitrated 3-methoxy-acenaphthenequinone, obtaining a mononitro derivative which was oxidised to the corresponding naphthalic anhydride. To establish the position taken up by the nitro group in the naphthalene nucleus, they attempted to remove the carboxyl radicals by distilling with soda-lime, but under these conditions extensive decomposition took place. However, they achieved the desired result in stages. The nitro-methoxy-naphthalic anhydride was mercurated according to the method of Leuck, Perkins and Whitmore (loc. cit.), and the resulting mercuration product was boiled with hydrochloric acid, when a nitro-methoxy-naphthoic acid was obtained. This acid was decarboxylated by dissolving in dry boiling quinoline and treating with copper bronze according to the method of Shepard, Winslow and Johnson (loc. cit.). In this manner, 6-nitro-2-methoxy-naphthalene was obtained, proving that the compound formed by the nitration of 3-methoxy-acenaphthenequinone was

7-nitro-3-methoxy acenaphthenequinone.



In this thesis the above method of decarboxylation has been applied with success to several other substituted α-naphthoic acids including the dinitro-derivative isolated by Pursell (p. 17).

Another use to which Ekstrand put the peri-amino-naphthoic acid was the preparation of naphtholactone. The amino-acid was dissolved in alkali, and diazotised by adding potassium nitrite and running the mixture slowly into ice-cooled dilute sulphuric acid. The solution was heated for some time and on cooling deposited needles, which proved to consist of naphtholactone. The lactone was dissolved in alkali and on acidification the hydroxy acid was precipiteted.



Ekstrand remarks that the ease with which the lactone

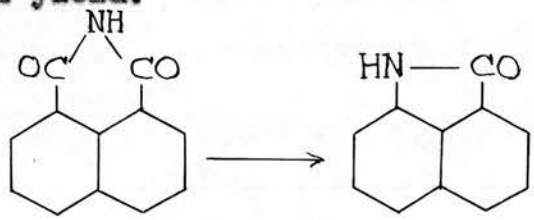
is formed from the diazo-derivative of the acid led to the expectation that the hydroxy acid would readily pass into the lactone, either by heating it alone or in solution in alcohol. This, however, was not found to be the case. The acid melted at 169° and on cooling re-melted about 130° - whereas the melting point of the lactone is 108°. Hence, even at 169° only a partial conversion into lactone was observed.

Ekstrand also prepared the monosubstituted bromo, chloro, and nitro-naphtholactones, but did not determine the position taken up by the entering groups. He converted these substituted lactones into the corresponding hydroxyacids by the same means as was used for the unsubstituted hydroxy acid, viz., dissolving the lactone in sodium hydroxide and precipitating the hydroxy acid by addification.

Up till the present time, naphthastyril has been very difficult to prepare in quantity. Ekstrand's method is long and only gives small yields. As described above, it consists of several stages:-
(1) nitration of α-naphthoic acid, followed by the tedious separation of the 5- and 8-nitro-acids,
(2) reduction of the 8-nitro-1-naphthoic acid to 8-amino-1-naphthoic acid, which on heating with water or alcohol is converted into naphthastyril (see p. 7).

A second method is given in a paper by Ullmann and Cassirer (Ber., 1910, 43, 439). These

authors converted naphthalimide into naphthastyril by means of the Hofmann reaction, that is, by treatment with sodium hypochlorite. However, this method also gives a small yield.



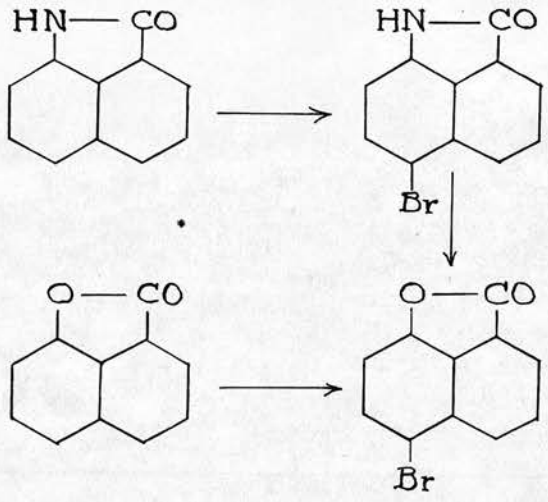

In addition to the preparation of such compounds as acetyl, benzoyl, and α- and β-naphthoyl-naphthastyrils, Ekstrand prepared several mono- and disubstituted naphthastyrils, the substituents being in the naphthalene nucleus. In all, he prepared three monosubstituted and three disubstituted naphthastyrils, viz., the mono-chloro, bromo, and nitro, and the dichloro, dibromo, and dinitro-derivatives. Since the mono-chloro, and bromo-naphthastyrils were prepared from known chloro- and bromo-naphthoic acids, their structures were readily deduced. The constitutions of the di-derivatives, however, were not established.

For example, on nitrating 5-chloro-1-naphthoic acid, Ekstrand obtained a nitro-chloro-naphthoic acid which on reduction with ferrous sulphate and ammonia yielded a chloro-amino acid. The latter on warming with alcohol split off water, giving an anhydride, which was therefore 5-chloro-naphthastyril (see p.16). Similarly, 5-bromo-naphthastyril was obtained from

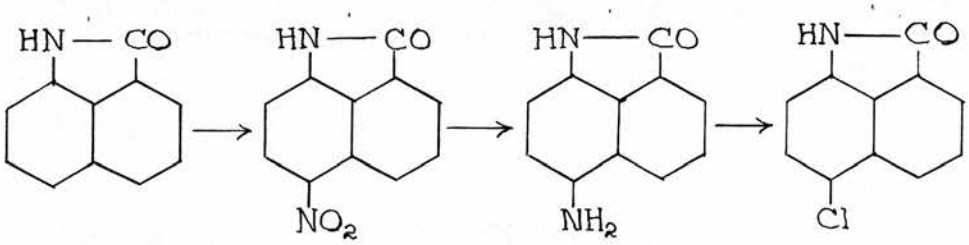
5-bromo-1-naphthoic acid.

The I. G. Farbenindustrie have recently patented a method for the preparation of 5-chloro-naphthastyril by the direct chlorination of naphth-astyril (see Zentralblatt, 1929, II, 1219). According to this method chlorine is passed into a solution of naphthastyril in concentrated sulphuric acid in presence of a little iodine at 15-20°. The solution is poured on ice and the precipitate filtered and recrystallised from glacial acetic acid.

Goldstein and Francey (Helv. Chim. Acta., 1932, XV, 1366) prepared 5-bromonaphthastyril by a modification of the I.G.F. method. They dissolved naphthastyril in glacial acetic acid, and by the addition of bromine precipitated the bromo-naphthastyril. In a further reaction this product was diazotised and the diazonium salt boiled with water. 5-Bromo-naphtholactone was thus isolated and shown to be identical with the unoriented compound prepared by Ekstrand by direct bromination of naphtholactone (p.20).



Turning once again to Ekstrand's work, this investigator prepared a mononitronaphthastyril by the direct nitration of naphthastyril in acetic acid solution with concentrated nitric acid. To determine the position of the nitro- group, he reduced the product with tin and hydrochloric acid to the corresponding amino-naphthastyril, which on diazotisation and treatment with a solution of cuprous chloride in hydrochloric acid, yielded the previously prepared 5-chloronaphthastyril. Hence the nitronaphthastyril had the nitro-group in position 5.




Ekstrand obtained dichloronaphthastyril by two methods. He heated 8-nitro-1-naphthoic acid in a sealed tube with fuming hydrochloric acid for two hours at 140-150°. The hydrochloric acid acted as a reducing as well as a chlorinating agent, the reaction being expressed by Ekstrand as follows:-

$$C_{10}H_6 \cdot NO_2 \cdot COOH + 6HCl \longrightarrow C_{10}H_6NH \cdot CO + 3H_2O + 3Cl_2$$

$$C_{10}H_6NH \cdot CO + 3Cl_2 \longrightarrow C_{10}H_4Cl_2NH \cdot CO + Cl_2 + 2HCl$$

No information, however, is given regarding the positions of the chlorine atoms. The second method was by the direct chlorination of naphthastyril - by treating an

aqueous suspension of naphthastyril with chlorine gas, the product being identical with the above.

Rule and Barnett (loc. cit.) found that on treating 8-nitro-1-naphthoic acid with thionyl chloride two reactions occurred simultaneously. On the one hand, chlorine displaced the nitro-group to form 8-chloro-1-naphthoic acid, and on the other, the reducing and chlorinating properties of the reagent converted some of the nitro-acid into dichloro-naphthastyril, the same product as was obtained by Ekstrand.

A dibromonaphthastyril was prepared by Ekstrand, using methods similar to those adopted for the preparation of the dichloro-derivative.

An interesting reaction was observed on dissolving this dibromonaphthastyril in fuming nitric acid. After standing for a day, yellow prisms separated out, which analysis proved to be dinitro-naphthastyril. Direct nitration of naphthastyril with fuming nitric acid, or 5-nitro-naphthastyril with concentrated nitric acid yielded dinitro-naphthastyrils which Ekstrand states are probably the same and identical with that obtained from dibromo-naphthastyril, although the melting points are too high to be accurately determined.

The following part of this thesis deals with the preparation and constitution of a number of compounds derived from α-naphthoic acid, naphtholactone, and naphthastyril.

## INDEX of PREPARATIONS.

# E X P E R I M E N T A L.

In the following pages the experimental work is described in detail and any discussion or conclusion arising from the work is introduced at its appropriate place in the text.

In all cases where new nitro-compounds were prepared, a nitrogen analysis was deemed sufficient for identification of the compound, because any possible variations in composition involved considerable differences in the nitrogen content. The preparations being carried out on a small scale, a micro-analytical method was employed. The micro-Dumas method, as developed by Pregl ("Manual of Organic Chemical Analysis", Thorpe and Whiteley, p. 233), which, in most cases, permitted analysis to be carried out on 10 to 20 milligrams of substance, gave results correct to within 0·20%.

The method employed for halogen estimation was that of Carius, the substance being heated with fuming nitric acid and silver nitrate in a sealed tube to 200-300°C, the halogen being obtained directly as silver halide.

## I. FURTHER SUBSTITUTION Of 8-BROMO-1-NAPHTHOIC ACID.

### A 1. Preparation of 5:X-dinitro-8-bromo-1-naphthoic Acid.

#### a. Preparation of 8-bromo-1-naphthoic acid.

α. Mercuration of naphthalic acid.

β. Bromination of the resulting anhydro-8-hydroxymercuri-1-naphthoic acid.

α. Ref:- Modified from Leuck, Perkin and Whitmore, J.A.C.S., 1929, 51, 1831.

Rule and Barnett, J.C.S., 1932, 179.

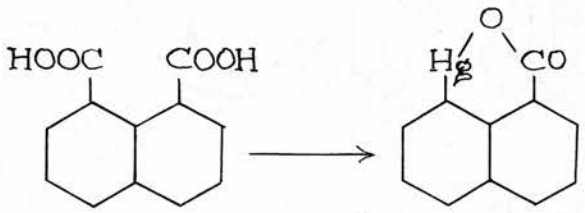
54 gms. naphthalic acid.

21 gms. sodium hydroxide.

55 gms. yellow mercuric oxide.

The naphthalic acid and sodium hydroxide were dissolved in 1200 c.c. water with heating. The resulting solution was filtered to remove insoluble impurity and placed in a 2 litre flask fitted with a reflux condenser. The yellow mercuric oxide was dissolved in a mixture of 50 c.c. glacial acetic acid with 150 c.c. water by warming slightly, and the resulting solution added to the flask. The contents of the flask were then made distinctly acid with acetic acid when a light brown suspension formed.

The contents of the flask were boiled for 96 hours till all carbon dioxide evolution ceased. A test portion then dissolved completely in aqueous sodium hydroxide and deposited no metallic mercury when treated with a clean copper wire. The flask was allowed to cool and the precipitate filtered off and washed successively with water, alcohol and ether. The product was then dried in a hot-air oven at 110-120°C. Yield, 83-85 grams, representing 97% of the theoretical.




Anhydro-8-hydroxy-mercuri-1-naphthoic Acid.

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β. Ref:- Modified from Whitmore and Fox., J. A.C.S., 1929, 51, 3363, by Davies, Heilbron and Irving, J.C.S., 1932, 2715.

80 gms. anhydro-8-hydroxy-mercuri-1-naphthoic acid.

34 gms. bromine.

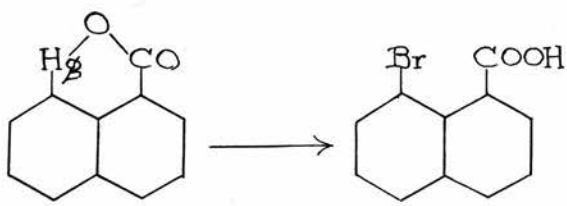
The mercuration product was suspended in 300 c.c. glacial acetic acid and 50 c.c. water added. The vessel containing the suspension was placed in an ice-bath and fitted with a mechanical stirrer. The

brominating solution was prepared by dissolving the liquid bromine in a concentrated solution of sodium bromide - approximately 150 c.c. This latter solution was added drop by drop to the rapidly stirred suspension over a period of two to three hours.

After the addition of the bromine, the mixture was slowly raised in temperature to 90-100°C with occasional stirring. A very small quantity of tar separated out, and the clear brown solution, after standing for 15 minutes at the above temperature, was poured into 2 litres of cold water. 8-Bromo-1-naphthoic acid separated as a pale yellow crystalline solid together with other slightly tarry materials. After standing overnight the solid was filtered off, washed with cold water, and extracted with 4-5 litres of boiling water from which, on cooling, the acid separated in a fairly pure state. This was filtered off, washed with cold water and dried at 100°.

The acid was then recrystallised from 250 c.c. benzene, when a product melting at 177-8° was obtained.

The yield was 33 gms. representing 57% of the theoretical.



b. 5-Nitro-8-bromo-1-naphthoic acid.

Ref:- W. Pursell (Ph.D. Thesis, Edinburgh, 1933).

10 gms. 8-bromo-1-naphthoic acid.
15 c.c. concentrated nitric acid.

The two acids were stirred to a cream in a wide-necked flask (250 c.c.). The flask was then placed on a water bath heated to 65° and shaken occasionally. A copious evolution of nitrous fumes took place and in 3-4 hours the reaction was complete. The contents of the flask were poured into 50 c.c. water, stirred and allowed to settle overnight. The light yellow product was filtered off, washed with cold water and dried in a steam oven. Weight, 10 gms.

The acid was purified by recrystallisation from a 1:1 mixture of alcohol and water. A yellow crystalline powder was obtained, melting at 247°. Yield, 7 gms.

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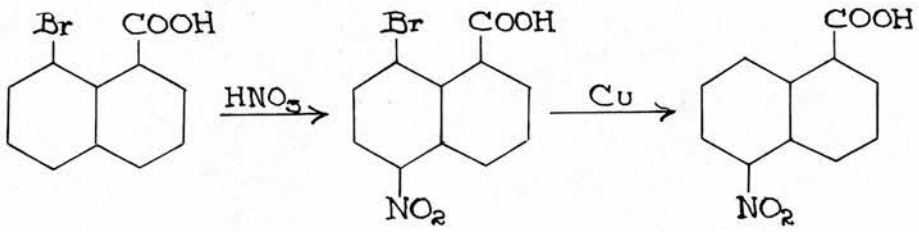
W. Pursell in these laboratories (loc. cit.) removed the bromine from this acid by boiling in dekalin or toluene suspension in presence of copper bronze, thus obtaining 5-nitro-1-naphthoic acid, and proving the above acid to be 5-nitro-8-bromo-1-naphthoic

acid.

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c. <u>5:X-Dinitro-8-bromo-1-naphthoic acid.</u>

Ref:- W. Pursell (Thesis, Edinburgh, 1933).

5 gms. 5-nitro-8-bromo-1-naphthoic acid.

8 c.c. nitration mixture.

The nitration mixture which gave the best results was found to be a mixture of 3 c.c. concentrated sulphuric acid, 4 c.c. fuming nitric acid and 4 c.c. concentrated nitric acid .

The halogenated acid was treated with the sulphuric-nitric acid mixture in a round-bottomed, wide-necked flask immersed in a boiling water bath for 2 hours; 2-3 c.c. of concentrated nitric acid were then added to prevent the mixture going dry, and the heating continued for 1 hour. The product was poured into water, allowed to stand overnight and filtered off. Weight, 5·7 gms.

The acid was difficult to recrystallise. A crystalline product was obtained by dissolving in boiling alcohol-water mixture (1:1) from which it separated on standing for a day. This product was again dissolved by warming in a 1:3 acetone-benzene mixture and thrown out by the addition of petrol ether, b.p. 80-100°. By this means the acid was obtained in needles melting at 249-252°, with decomposition.

W. Pursell proved by analysis that this acid was a dinitro-bromo-naphthoic acid.

The present writer found two simpler and better methods for purifying this acid than that quoted above. (1) The acid was boiled under reflux for 2 hours with 15 c.c. benzene (A.R.). The mixture was filtered hot when the purified dinitro-bromo-acid was retained on the filter paper, it being insoluble in benzene. Finally, the acid was washed with a little cold benzene and then with petrol ether and dried. The product melted at 250-252° (decomp.). (2) Recrystallisation from concentrated nitric acid yielded yellow needles of the above quoted melting point.

The 5-nitro-8-bromo-1-naphthoic acid was used direct from the nitration of 8-bromo-1-naphthoic acid without further purification, because it was found that this procedure gave a larger percentage yield of end-product based on the weight of 8-bromo-1-naphthoic acid employed as starting material.

Yield, 3·2 gms., representing 56% of the theoretical, calculating from the impure 5-nitro-8-bromo-1-naphthoic acid, or 33% of the theoretical, calculating from the 8-bromo-1-naphthoic acid.

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A 2. Determination of the Constitution of the above 5:X-dinitro-8-bromo-1-naphthoic acid.

As this acid was prepared by the nitration of 5-nitro-8-bromo-1-naphthoic acid, it only remained to show the position of the second nitro group, designated by X.

a. Attempted removal of the carboxyl group by heating.

As the acid decomposes at its melting point it was thought that perhaps the carboxyl group might be removed by heating to give a dinitro-bromo-naphthalene.

2 gms. of the acid were placed in a test-tube and heated in an oil bath at 290° for about 1 hour. The acid melted, then darkened in colour and frothed. On cooling, it was found that the contents of the tube were black and carbonaceous. The black material was heated with sodium hydroxide to remove unchanged acid, and then filtered. The filtrate on acidification

deposited a brown coloured solid, which however was not further examined except to prove its acidic character.

The alkali insoluble residue was washed with water and dried. It proved, however, to be carbon.

Varying the time of heating gave no improvement.

Apparently the decomposition not only involves the loss of carbon dioxide due to the removal of the carboxyl group, but also a complete disruption of the molecule.

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b. <u>Attempted removal of the carboxyl group, using the "copper-quinoline" method.</u>

Ref:- Shepard, Winslow and Johnson (loc. cit.)
Davies, Heilbron and Irving (loc. cit.)

0·5 gms. 5:X-dinitro-8-bromo-1-naphthoic acid.

1 c.c. dry quinoline.

0·25 gms. copper bronze.

The quinoline was boiled under reflux in a 10 c.c. round-bottomed flask immersed in a small oil bath, and the acid added. The copper bronze was then carefully introduced in small portions. The contents of the flask frothed and darkened in colour, and the

quinoline was maintained at the boiling point for 15 minutes after the addition of the copper.

The cold product was extracted with ether, the ether extract washed with dilute hydrochloric acid to remove quinoline, then with aqueous sodium carbonate and finally with water. On removal of the ether by evaporation, however, only a very small amount of a dark red sticky substance was left, which was not further examined.

The contents of the flask were then extracted with acetone, filtered, and the filtrate boiled with animal charcoal. The acetone was removed by evaporation, leaving a black residue. This substance was dissolved in boiling alcohol which, on cooling, deposited a brown solid.

A melting point of this product was taken - it darkened about 150° and melted with decomposition from 160-170°. It was insoluble in alkali but was too small in quantity to purify further.

The melting point might suggest that the product was 1-bromo-4:5-dinitronaphthalene, for which the quoted melting point is 170°. (Van der Kam, "Naphthalin Derivate").

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As this method proved unsatisfactory it was

decided to repeat the decarboxylation after first removing the halogen atom in position 8.

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c. Dehalogenation of 5:X-dinitro-8-bromo-1-naphthoic acid.

Ref:- W. Pursell (loc. cit.)

2 gms. 5:X-dinitro-8-bromo-1-naphthoic acid.

2 gms. copper bronze.

15 c.c. toluene.

The acid, copper and toluene were placed together in a 100 c.c. bolt-head flask fitted with a reflux condenser, and heated for 7 hours in a small oil bath so that the toluene boiled vigorously.

The copper soon lost its bright appearance and a brownish deposit was formed.

The contents of the flask were then warmed with sodium hydroxide solution, and the mixture filtered into a separating funnel. The lower aqueous layer was separated from the toluene, and acidified with nitric acid, when a dark brown precipitate of the reduced acid was obtained. After allowing to settle for a few hours it was filtered off, washed with cold

water and dried. Weight, 1·32 gms.

The crude product was dissolved in boiling aqueous alcohol (1:1) and boiled for a few minutes with animal charcoal. The liquid was filtered and on cooling crystals of the acid appeared. The crystals were colourless needles as seen under the microscope, but in bulk the acid was a buff coloured powder. Yield, 0·72 gms. M.p., 257-259°.

Pursell proved by a nitrogen analysis that this was a dinitro-naphthoic acid.

The yield of purified product quoted above is 47% of the theoretical.

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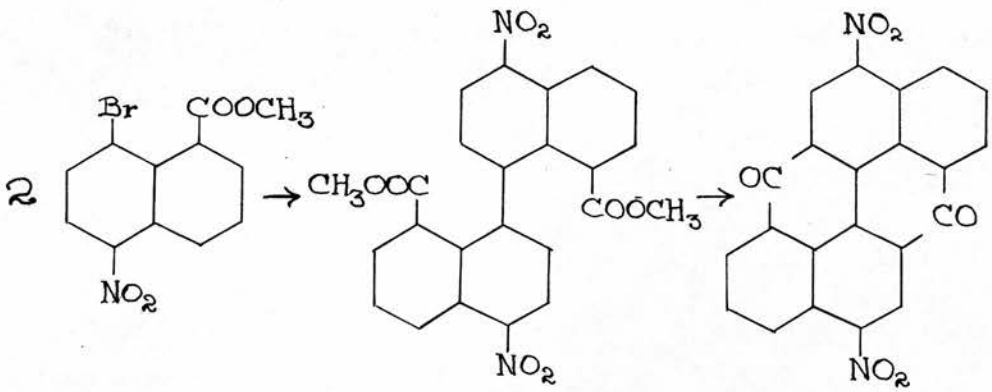
Since the compound under consideration was prepared by the further nitration of 5-nitro-8-bromo-1-naphthoic acid, it is evident that the only possible positions for the second nitro group to enter are 7, 6, 4, 3, or 2. Now from general considerations of the orientation of entering groups in the naphthalene nucleus it will be seen that positions 2, 3, and 6 are highly improbable, so that the most probable positions

are 4 and 7.

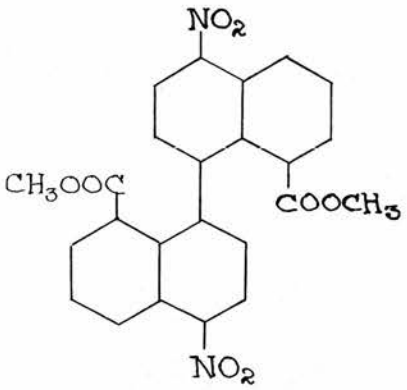
Physical evidence obtained by W. Pursell (loc. cit.) led to the conclusion that the second nitro group in 5:X-dinitro-8-bromo-1-naphthoic acid occupied the 7-position. The physical evidence being as follows: (1) It was found that dimethyl-4:4':X:X'-tetranitro-1:1'-dinaphthyl-8:8'-dicarboxylate obtained by coupling two molecules of methyl-5:X-dinitro-8-bromo-1-naphthoate did not give a tetranitro-anthanthrone on being heated with concentrated sulphuric acid. This can be readily explained if the 2:2' positions are occupied by nitro groups, that is, if the second nitro group occupies the 7-position in the dinitro-bromo-acid. The dinitro-dinaphthyl carboxylic acid has been shown to form the anthanthrone.



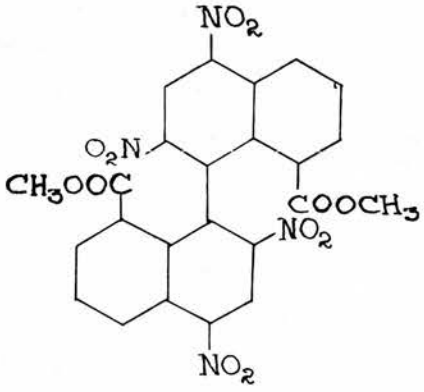

Dinitro-anthanthrone

(2) In comparing the rates of hydrolysis of the dimethyl esters of 4:4'-dinitro-1:1'-dinaphthyl-8:8'-dicarboxylic acid and the related tetranitro acid it was found that the tetranitro ester (II) was much more

difficult to hydrolyse than the dinitro ester (I). This is also readily explained if the 2:2' positions in the tetranitro ester are occupied by nitro groups, being then a steric hindrance effect.



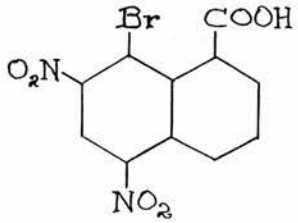

I




II

(3) The increased reactivity of the halogen atom in the dinitro-bromo-acid as compared with the mononitro-bromo-acid similarly led to the conclusion that the former has the second nitro group in the 7-position.

The above evidence would therefore indicate the following structure for the dinitro-bromo-acid.




This discussion will be found to rest almost entirely upon the physical properties of the naphthalene ring, that is, upon spatial and transmitted effects in the molecule, the study of which up to the present has not reached any degree of finality.

If the conclusion derived from the above physical evidence is correct, the acid obtained by the dehalogenation of the dinitro-bromo-acid (p. 38) must be 5:7-dinitro-1-naphthoic acid. This acid is not mentioned in the literature. Ekstrand, however, prepared 4:5-dinitro-1-naphthoic acid (J. pr., [2], 1888, 38, 256) which melts at 265°, approximating closely to that obtained for 5:X-dinitro-1-naphthoic acid, namely, 257-259° (p. 39). Pursell prepared ethyl-5:X-dinitro-1-naphthoate and found that it melted at the same temperature as quoted by Ekstrand for ethyl-4:5-dinitro-1-naphthoate, namely, 143°. Although these melting points are very close together, the evidence cannot be taken as definitely proving the 4:5-structure.

It was thought that if the above 5:X-dinitro-1-naphthoic acid could be decarboxylated and the resulting dinitro-naphthalene identified, the position of the second nitro group would be settled.

d. Decarboxylation of 5:X-dinitro-1-naphthoic acid.

0·5 gms. 5:X-dinitro-1-naphthoic acid

1 c.c. dry quinoline.

0·25 gms. copper bronze.

The quinoline was boiled under reflux in a 10 c.c. round-bottomed flask, the flask being heated in a small oil bath.

The acid was added to the quinoline in which it dissolved, and the copper was then carefully introduced into the boiling solution. The contents of the flask frothed and darkened, heating being continued for 15 minutes after the addition of the copper.

After cooling, the product was extracted with ether. The ether extract was washed with dilute hydrochloric acid to remove quinoline, then with aqueous sodium carbonate and finally with water. The solution was dried by standing over calcium chloride. The ether was removed by evaporation, and the resulting brownish coloured residue recrystallised twice from benzene.

In bulk the product appeared as pale brownish coloured plates which under the microscope proved to be colourless rhombic plates. It was non-acidic and was presumably a dinitro-naphthalene.

Yield, 0·15 gms. representing 36% of the theoretical. The product melted at 166-169°.

This melting point eliminates all the dinitro-naphthalenes except the 1:6 and 1:8 isomers, the melting point of the former being quoted as 166° and of the latter 167° and 170° (see Van der Kam, "Naphthalin Derivate"). The 1:3 isomer which corresponds to the 5:7-dinitro-1-naphthoic acid melts at 144°.

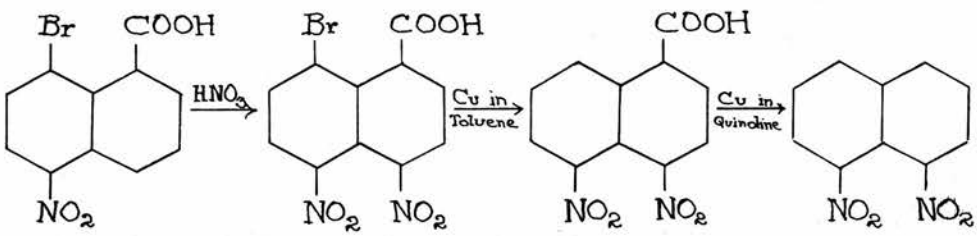
A mixed melting point with an authentic specimen of 1:8-dinitro-naphthalene (B.D.H. product recrystallised from chloroform) was taken.

| | |
|---|---|
| Melting point of 1:8-dinitronaphthalene, | 167° |
| " " " 1:X-dinitronaphthalene, | 166-169° |
| " " " mixture, | 167-169° |

No depression of the melting point was observed, and it was therefore concluded that the 1:X-dinitro-naphthalene was the 1:8 isomer.

It was further observed that both dinitro - naphthalenes had the same crystalline form, namely, rhombic plates.

Tracing this back, the dinitro-naphthoic acid is thus 4:5-dinitro-1-naphthoic acid which was obtained from a dinitro-bromo-naphthoic acid, which must therefore be 4:5-dinitro-8-bromo-1-naphthoic acid. These conclusions are summarised in the following scheme:

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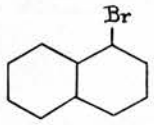
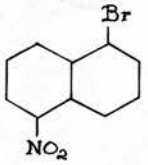
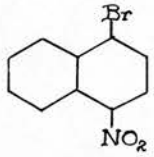
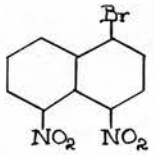
DISCUSSION.

It is difficult to discuss the foregoing physical evidence for the 5:7 structure in the light of the above result, since very few compounds of a similar type have been studied.

The observed reactivities of the nitro-bromo-acids are in keeping with certain observations made by Salkind (Ber., 1931, 64, 289). He studied, amongst other reactions, the reaction between α-bromonaphthalene and several of its nitro-derivatives and piperidine at various temperatures. In general, he found that the reactivity of the bromine was increased if the nitro-group was in the same ring as the bromine (1-nitro-4-bromonaphthalene) as compared with the case in which the nitro group was in the other ring (1:5 isomer), which was not much more reactive than α-bromonaphthalene itself. However, in the case of 1:8-dinitro-4-bromo-

naphthalene the reactivity of the bromine was very much greater than even in 1-nitro-4-bromonaphthalene. The following table summarises his results at 50-60°, giving the percentage reacting in 24 hours.

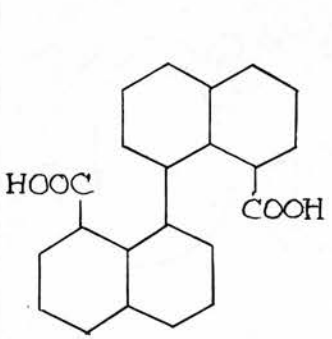
| Substance | % | Substance | % |
|---|---|---|---|
|  | No reaction |  | 7·79 |
|  | 58·87 |  | 96·22 |

Thus the observation that the bromine atom in 4:5-dinitro-8-bromo-1-naphthoic acid is much more reactive than that in 5-nitro-8-bromo-1-naphthoic acid is to be expected from a consideration of Salkind's results.

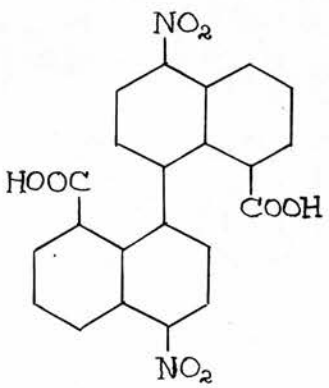
The steric effect observed in the case of hydrolysis of the dinaphthyl ester cannot be readily explained and will have to be left meanwhile as a fact until the hydrolysis of esters of similar configuration has been studied.

The failure to obtain the tetranitro anthanthrone is also difficult to explain since the 2:2' positions are unoccupied. It may be that the conditions

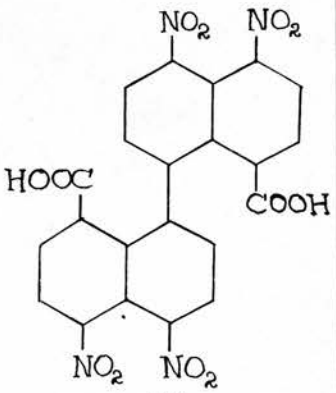
employed to effect ring closure break down the molecule, the tetranitro acid being somewhat unstable at 160°; experimentally such decomposition was observed. On the other hand, the introduction of the nitro groups into the dinaphthyl acid may deactivate the molecule in such a way as to hinder or prevent ring closure. Thus, in the case of the dinitro-dinaphthyl-dicarboxylic acid (II) it has been observed that ring closure to form the corresponding anthanthrone does not take place so readily as with the unsubstituted dinaphthyl-dicarboxylic acid (I). Hence it is possible that in the case of the tetranitro acid (III) the molecule is so deactivated that ring closure cannot be effected under the conditions employed.




I




II

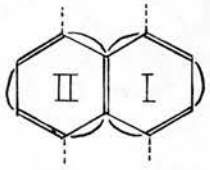



III

Although much qualitative information is to hand dealing with substitution in the naphthalene molecule, at present only homonuclear substitution has been studied to any great extent from a theoretical point of view. So that meanwhile, although analogies can

be drawn from similar cases, the orienting influence of groups in naphthalene derivatives cannot be discussed on any sound theoretical basis.

Thiele's theory of partial valencies, although much criticised of recent years, gives a ready explanation for the exclusive formation of α-monosubstituted derivatives, there being, according to this theory, 'half' partial valencies situated on the α-positions, the molecule being a system of conjugated double bonds.




These partial valencies coupled with the 'accelerative' or 'retarding' influence of other groups present may account for at least some of the observed facts (see Holleman, Chemical Review, 1924, p. 187).

Thus, if position 1 be occupied by a carboxyl group, a substituent which slows up further substitution in the ring, the conjugated system in ring I is deactivated; thus the most favourable positions for further substitution are 5 and 8 due to the partial valencies on these positions, with a probable preponderance of the 5 isomer, owing to the steric hindrance of the carboxyl group exerted towards position 8. This is borne out in practice (see Ekstrand's work on nitration of α-naphthoic acid,

Introduction, pp. 7 and 13).

If positions 1, 5 and 8 be occupied as in 5-nitro-8-bromo-1-naphthoic acid, the conjugated system in ring II is deactivated by the two deactivating substituents Br and $NO_2$, thus retarding further substitution in that ring. Likewise, the conjugated system in ring I is deactivated by the carboxyl group; however, this influence is apparently overcome by the partial valence on position 4, because on further nitration 5-nitro-8-bromo-1-naphthoic acid yields 4:5-dinitro-8-bromo-1-naphthoic acid.

However, since no completely analagous case is known, the above consideration is somewhat conjectural although supported by the actual case in point.

---

## B 1. Bromination of 8-Bromo-1-naphthoic Acid.

Several attempts were made to brominate 8-bromo-1-naphthoic acid before suitable conditions were found. These are given in brief below.

a. 2 gms. of 8-bromo-1-naphthoic acid were suspended in 20 c.c. carbon tetrachloride. 0·7 c.c.

bromine was added from a graduated pipette (about 50% excess). The flask was placed in a water bath and the contents boiled for 3 hours.

The colour of bromine had not disappeared. The contents of the flask were filtered and the product washed with carbon tetrachloride and benzene, then dried. It proved to be unchanged 8-bromo-1-naphthoic acid.

---

b. The above experiment was repeated, using 20 c.c. glacial acetic acid instead of carbon tetrachloride, the bromo-acid being in solution instead of suspension. The contents of the flask were heated to 70° for 3 hours; however, the bromination again failed, the starting product being recovered unchanged.

---

c. Experiment b. was repeated, but the contents of the flask were boiled for 4 hours.

The solution was poured into 50 c.c. of cold water when a greyish solid separated out. After standing overnight the product was filtered, washed with cold water and dried.

The product, after recrystallisation, melted over a range of several degrees about 170°. A mixed

melting point with pure 8-bromo-1-naphthoic acid showed no depression. The product was apparently unchanged bromo-acid contaminated with probably a small amount of a higher bromo-compound, which accounts for the low melting point.

---

d. 2 gms. 8-bromo-1-naphthoic acid, 5 c.c. glacial acetic acid and 0·7 c.c. bromine were sealed off in a 1-foot length of combustion tubing. The tube was placed in an asbestos box and the temperature slowly taken up to 150-160°, at which temperature it was maintained for 4½ hours.

When cold, the tube was opened; white fumes of hydrobromic acid appeared, but there was no sign of bromine although the acetic acid was red in colour. Crystals had deposited from the acetic acid.

The contents of the tube were poured into about 20 c.c. cold water. After standing overnight, the greyish-red product was filtered off, washed with cold water and dried.

The substance was dissolved in aqueous sodium carbonate, and filtered to remove neutral impurity. The filtrate was acidified with hydrochloric acid and allowed to stand for a few hours. The precipitate was filtered, washed with water and dried in an oven at 100°.

It was repeatedly recrystallised from absolute alcohol until the maximum melting point was obtained, namely 232°.

In bulk the product was a crystalline solid with a very pale reddish tint. Under the microscope it appeared as colourless plates.

The yield was 0·6 gms., being much diminished by repeated recrystallisation.

---

e. d. was repeated, but the heating was only continued for 2½ hours after the temperature of 150-160° had been reached.

A yield of 1·68 gms. was obtained, the product melting at 232°.

---

Bromine analysis (Carius).

Calculated for 8:X-dibromo-1-naphthoic acid = 48·5%

Found = 48·7%

The product is therefore a dibromo-naphthoic acid, none of which were listed in the literature.

The above preparation e. was transferred to a larger scale.

10 gms. 8-bromo-1-naphthoic acid.

25 c.c. of a 10% solution of bromine in acetic acid. (volume).

The bromo-acid and brominating solution were heated together at 150-160° for 2½ hours in a sealed tube. On cooling, the tube was opened, white fumes of hydrobromic acid were evolved, but no bromine appeared to be present.

The crystals which had separated out were filtered off, and the filtrate set aside for further examination. The crystalline solid was washed with water and dissolved in sodium carbonate, filtered from neutral impurity and reprecipitated with hydrochloric acid. The precipitate which was pale pink in colour was washed with water, dried and recrystallised from 75 c.c. absolute alcohol. Pale pink crystals were obtained which appeared as colourless plates under the microscope and melted at 232°. Weight, 7·3 gms.

The acetic acid mother liquor from the bromination was treated with a large volume of water, when a reddish-coloured precipitate formed. After standing for some time, the precipitate was filtered off and wahhed with water. The solid was boiled out with 100 c.c. water and filtered; the filtrate on cooling deposited white plates. These plates were recrystallised from benzene. The recrystallised product melted at 177-179°. A mixed melting point proved it

to be 8-bromo-1-naphthoic acid. Weight, 1 gm.

The above yield of dibromo-acid represents 62% of the theoretical, allowing for recovered starting material.

---

## B 2. Determination of the Constitution of the above 8:X-Dibromo-1-naphthoic Acid.

No dibromo-naphthoic acids were listed in the literature up to this time, so the product could not be identified directly.

As the acid was prepared by the direct bromination of 8-bromo-1-naphthoic acid, only the position of the second bromine atom requires to be shown, designated meanwhile for convenience as X.

Since 8-bromo-1-naphthoic acid nitrates in the 5 position, it is probable that it also brominates in the same position. If this is so, the above acid will be 5:8-dibromo-1-naphthoic acid, so that if the bromine in the 8-position be removed the product obtained would be 5-bromo-1-naphthoic acid which is known.

Dehalogenation of 8:X-dibromo-1-naphthoic acid by means of copper bronze.

0·5 gms. 8:X-dibromo-1-naphthoic acid.

0·5 gms. copper bronze.

5 c.c. toluene.

The acid, copper and toluene were placed in a 100 c.c. bolt-head flask fitted with a reflux condenser and heated in a small oil bath at 120-130° for 2½ hours.

The copper soon lost its bright appearance and a yellowish-brown deposit formed.

The contents of the flask were warmed with sodium hydroxide solution and filtered into a separating funnel. The lower aqueous layer was separated from the toluene, and acidified with hydrochloric acid, when a yellowish precipitate formed. After standing overnight, the precipitate was filtered off, washed with water and dried in a steam oven. It was recrystallised twice from absolute alcohol from which it separated as white needles, melting at 257°.

Weight, 0·25 gms.

A mixture of this acid and pure 5-bromo-1-naphthoic acid (m.p. 260°) melted at 258°, thus proving that this compound was 5-bromo-1-naphthoic acid.

The above yield represents 66% of the theoretical.

It is therefore evident that the acid from which

the 5-bromo-1-naphthoic acid was obtained was 5:8-dibromo-1-naphthoic acid.

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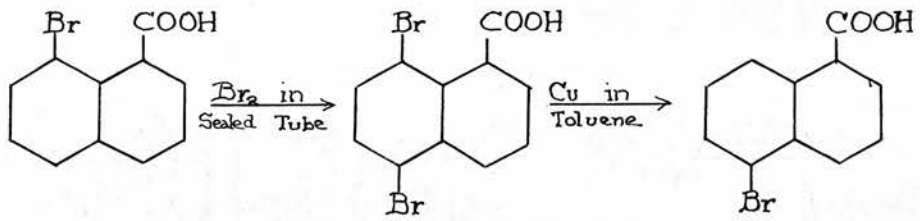
Summary.

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DISCUSSION.

This experimental result was to be expected from the behaviour of 8-bromo-1-naphthoic acid on nitration, when the nitro group enters the 5-position. It is also in keeping with the foregoing theoretical considerations (p. 48). In 8-bromo-1-naphthoic acid the conjugated systems in both rings are deactivated, due to the presence of the deactivating substituents Br and COOH. However, it is an observed fact, in the benzene series at least, and therefore probably for all homonuclear substitution, that the presence of a substituent group containing double bonds, such as the carboxyl group, increases the difficulty of

further substitution, whereas substituents containing single linkages, such as Br, although they may be deactivating groups, do not retard further substitution to the same degree. ($-NH_2$ , -OH, and $-OCH_3$ are activating groups). Thus on nitration or bromination, 8-bromo-1-naphthoic acid substitutes in the 5-position.

The effect of a substituent on further substitution in the same ring can be predicted with reasonable certainty, but meanwhile no inference regarding its effect on substitution in the other ring can be drawn, apart from either favouring or preventing substitution in the same ring and thereby making further substitution in the other ring either less or more probable.

When this work was completed (November 1932) there appeared a paper in the November issue of Helvetica Chimica Acta (vol. XV) by Goldstein and Francey reporting the preparation of 5:8-dibromo-1-naphthoic acid from 5-bromonaphthastyril. They diazotised 5-bromonaphthastyril and treated the diazo salt solution with cuprous bromide. These authors quote a melting point of 227·5°, as compared with 232° above. They characterised this acid by the preparation of its methyl and ethyl esters.

---

## B 3. Attempted Bromination of 5:8-dibromo-1-Naphthoic Acid.

No success attended the efforts to introduce another bromine atom into 5:8-dibromo-1-naphthoic acid, so the work on this subject is only given briefly.

a. The dibromo-acid, 2 gm., was boiled under reflux for 4 hours in solution in 25 c.c. glacial acetic acid in presence of a little iodine and 1 c.c. of bromine.

On cooling, a white crystalline sold separated which was filtered off, washed with a little cold acetic acid and dried. The product melted at 230-232°, and on admixture with pure 5:8-dibromo-1-naphthoic acid gave no depression of the melting point. It was unchanged dibromo-acid.

---

b. The bromination was attempted by heating 1 gm. of the dibromo acid with 0·5 gm. bromine and 5 c.c. glacial acetic acid at 170-180° in a sealed tube for 3 hours. After this treatment there was still unchanged bromine in the tube.

When cold, the crystals which had separated were filtered off, washed with a little acetic acid, then water, and dried. There was very little evidence of hydrobromic acid having been formed.

The product crystallised from acetic acid as white

needles or long narrow plates. A mixed melting point proved that it was recovered dibromo-acid.

---

c. The above experiment b was repeated with the addition of 0·25 gm. anhydrous ferric chloride as catalyst, but the result was the same as in b.

---

d. The dibromo-acid, 1 gm., was heated with 0·5 gm. bromine in a sealed tube at 170-180° for 6 hours, no solvent being present.

On cooling, the colour of the bromine had gone, and when the tube was opened there was a great release of pressure, and white fumes of hydrogen bromide were emitted.

The solid was extracted with sodium carbonate, and the insoluble portion recrystallised from absolute alcohol. It melted over a few degrees at about 169°, but this was not improved by further recrystallisation. The compound contained bromine, but being insoluble in sodium carbonate, it was not an acid.

Analysis. Bromine by Carius Method.

| | |
|---|---|
| Found, | 67·5% |
| Calculated for tribromonaphthalene, | 65·7% |

The product was apparently a mixture of tribromo-

and tetrabromo-naphthalenes.

On acidifying the sodium carbonate extract, a small amount of the original dibromo-acid was recovered.

Since decarboxylation had occurred in the above reaction, the increased pressure was due - in part - to carbon dioxide.

---

e. Experiment d. was repeated but the tube was only heated to 100°. The result, however, was the same as in d. with less of the neutral product and a greater proportion of recovered dibromo-acid.

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## II A. THE PREPARATION of 8-HYDROXY-1-NAPHTHOIC ACID And Its CONVERSION To NAPHTHOLACTONE.

### 1. Preparation of 8-Hydroxy-1-naphthoic Acid.

General Method.

The 8-bromo-1-naphthoic acid was dissolved in aqueous sodium hydroxide and copper bronze added. After boiling under reflux for two hours, the dark solution was filtered, when cold, through a sintered glass filter to remove the copper. As the copper functioned as a catalyst it remained untarnished. The copper was washed with a little water.

The filtrate was acidified with hydrochloric acid, when a buff-coloured precipitate formed which became granular on standing overnight. It was observed that a dark tarry precipitate was obtained when nitric acid was used for acidification.

On filtering the precipitate and drying it at 100°, the colour changed from buff to yellow. The solid was dissolved in cold ether, filtered to remove the small amount of insoluble residue, and the ether removed by evaporation. The yellow product was re-crystallised from ligroin, from which it separated as bright yellow micro-crystalline needles.

This substance contained no halogen, as tested for by Beilstein's copper wire test. It was acidic and was also a hydroxy compound giving a purple colour with ferric chloride - it was 8-hydroxy-1-maphthoic acid.

Several experiments were carried out to determine conditions to give the maximum yield. Various concentrations of sodium hydroxide were employed and varying amounts of catalyst. In each case 2 gms. of 8-bromo-1-naphthoic were used, the volume of the solutions being 50 c.c. Approximately 200 c.c. of ligroin were required in each case for the recrystallisation.

The results are summarised in the following table.

| No. | Normality of NaOH | Wt. of Cu. | Yield gms. | Yield % | M.p. |
|---|---|---|---|---|---|
| 1 | 1 | 0·2 gm. | 0·75 | 50 | 169° |
| 2 | 2 | " | 0·79 | 53 | " |
| 3 | 4 | " | 0·78 | 52 | " |
| 4 | 8 | " | 0·75 | 50 | " |
| 5 | 2 | 1·0 gm. | 0·86 | 58 | " |
| 6 | 4 | " | 0·82 | 55 | " |

Although the differences in the yields are too small to allow any definite conclusions to be made, being within the experimental error, it seems that the maximum yield is obtainable with 2 N sodium hydroxide, the yield being smaller with either more dilute or more concentrated alkali.

A somewhat greater yield appears to be given when the proportion of catalyst is increased, probably due to the greater active surface.

---

From a consideration of Ekstrand's work on this subject (see Introduction, p. 19) it was to be expected that the above preparation should yield the hydroxy-acid and not naphtholactone. He obtained the lactone from the amino-acid by diazotisation and boiling the diazonium salt with water. The lactone was converted to the hydroxy acid by dissolving in sodium hydroxide and precipitating the hydroxy acid by acidification, which part of his work is comparable with the above preparation of the hydroxy acid.

As stated in the Introduction, although Ekstrand found that the lactone could be readily converted into the hydroxy-acid, he was not able to effect the reverse transformation. The following experiments were therefore carried out for the purpose of determining the best conditions for this change.

## 2. Conversion of 8-Hydroxy-1-naphthoic Acid to Naphtholactone.

a. Half a gramme of the hydroxy acid was dissolved in ligroin, and two-thirds of the ligroin distilled off. By this means it was hoped to remove water from the hydroxy acid and so obtain the lactone. However, on cooling, the hydroxy acid was deposited and not the lactone.

---

b. 2 gms. 8-hydroxy-1-naphthoic acid
2 gms. phosphorus pentoxide
100 c.c. benzene.

The hydroxy-acid was dissolved in the boiling benzene. After the addition of the phosphorus pentoxide the product was boiled under reflux for two hours. The phosphorus pentoxide remained in suspension and became dark in colour as the boiling continued. After settling for a few minutes the benzene was decanted off from the solid material.

When cold, no solid deposited from the solution, so most of the benzene was distilled off and then completely removed in a vacuum desiccator. A mass of yellow needles was left.

This product was treated with cold dilute sodium carbonate to remove free acid, filtered, washed with water and dried in a vacuum desiccator. The neutral solid was recrystallised from ligroin, from which it crystallised in yellow needles, melting at 108°. A mixed melting point with naphtholactone prepared by Ekstrand's method was taken. No depression of the melting point was observed, thus proving the product to be naphtholactone.

Yield, 0·6 gms.

The sodium carbonate extract was acidified whereby 0·35 gms. of hydroxy acid was recovered.

The above quoted yield is therefore 40% of the theoretical.

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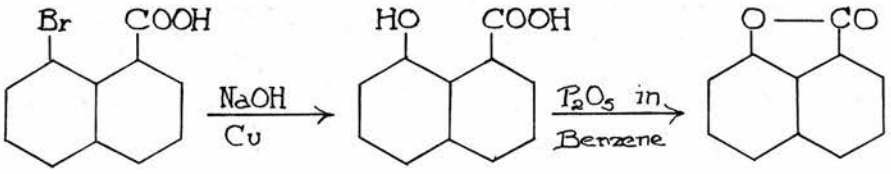


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c. Experiment b. was repeated, using anhydrous copper sulphate in place of phosphorus pentoxide, but no lactone was obtained, the hydroxy acid being recovered.

---

## 3. The Determination of the Constitution of Substituted 8-Hydroxy-1-naphthoic Acids.

Ekstrand (loc. cit.) prepared a mononitro- and a mono-bromo-derivative of naphtholactone by direct nitration and bromination respectively, and from these obtained the corresponding nitro- and bromo-hydroxy acids, but he did not determine the positions of the substituent groups (see Introduction, p. 20).

It was desired to find a means of orienting derivatives of 8-hydroxy-1-naphthoic acid. Three possible ways presented themselves and these were tried out on unsubstituted 8-hydroxy-1-naphthoic acid.

---

### a. Reaction between 8-hydroxy-1-naphthoic acid and phosphorus pentabromide.

It was thought that if the hydroxyl group could be replaced by bromine, substituted 8-bromo-1-naphthoic acids would be obtainable from substituted 8-hydroxy-1-naphthoic acids, which might correspond with those of known constitution prepared already by direct substitution of 8-bromo-1-naphthoic acid.

0·5 gm. 8-hydroxy-1-naphthoic acid

8 gms. phosphorus pentabromide

The hydroxy-acid and phosphorus pentabromide were

heated together on an oil bath at 150° in a 100 c.c. flask fitted with a ground-in reflux air condenser.

After about quarter of an hour, a vigorous reaction set in, bromine fumes were evolved and orange-coloured needles sublimed on to the cooler surface of the flask, leaving a dark oil at the bottom.

When cold, water was carefully added and a vigorous reaction took place, hydrogen bromide being evolved. Water was added until all the reaction had ceased. A reddish-brown solid separated which, after standing overnight, was filtered off. It was boiled out with sodium carbonate, filtered, washed with water and dried. The final product was still coloured red.

On acidfying the sodium carbonate extract only a very faint precipitate was obtained, too small in quantity to examine further. Evidently the bulk of the yield was in the red-coloured solid which was not a free acid.

The product was boiled out twice with animal charcoal in acetic acid. From the acetic acid, on cooling, fine white needles deposited.

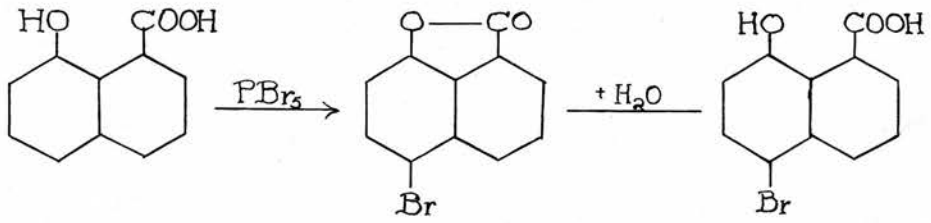
Weight, 0·3 gm. M.p., 189-192°.

Beilstein's copper wire test proved that the compound contained halogen. It was insoluble in sodium carbonate, so was not an acid. However, it dissolved in boiling sodium hydroxide, which solution when acidified gave a precipitate which was then soluble in sodium carbonate.

The substance was 5-bromonaphtholactone. Ekstrand (loc. cit.) quotes 192° as the melting point of a bromonaphtholactone, which Goldstein and Francey (loc. cit.) have recently proved to be 5-bromo-naphtholactone. (see Introduction, pp. 20 and 22).

Sodium carbonate is unable to open the lactone ring, but sodium hydroxide can open it with the formation of the sodium salt of the hydroxy-acid. The sodium hydroxide solution, when acidified, gives a precipitate of 5-bromo-8-hydroxy-1-naphthoic acid which is soluble in sodium carbonate.

The yield of 5-bromonaphtholactone quoted above represents 46% of the theoretical.




insoluble in $Na_2CO_3$ soluble in $Na_2CO_3$

---

Hence phosphorus pentabromide cannot be used to prepare substituted 8-bromo-1-naphthoic acids from substituted 8-hydroxy-1-naphthoic acids.

---

b. Attempted decarboxylation of 8-hydroxy-1-naphthoic acid.

If the substituted 8-hydroxy-1-naphthoic acids could be decarboxylated, substituted α-naphthols would be obtained which could probably be identified.

8-Hydroxy-1-naphthoic acid (0·5 gm.) was dissolved in 1 c.c. of dry boiling quinoline and 0·25 gm. copper bronze added, the heating being continued for 15 minutes as in previous experiments (see p. 43).

When cold, the product was extracted with ether, the ether solution being washed with dilute hydrochloric acid, sodium bicarbonate and finally water. After drying over anhydrous sodium sulphate, the solvent was removed by evaporation. The resulting yellow solid which had a decided smell of α-naphthol was recrystallised from ligroin from which it separated in fine needles.

Yield, 0·2 gm. M.p., 108°.

This substance, however, proved to be naphtholactone and not α-naphthol.

It was observed in the preparation of the hydroxy-acid from the bromo-acid that there was a decided smell of α-naphthol, evidently a slight heat decomposition. Similarly, in the above reaction, although there was a smell of α-naphthol, insufficient was present to separate. Apparently the bulk of the hydroxy-acid does not lose carbon dioxide by the above method -

only water is split off to yield the lactone.

The recovered lactone represents 44% of the starting material.

---

The "copper-quinoline" method therefore cannot satisfactorily be used to decarboxylate substituted 8-hydroxy-1-naphthoic acids, possibly because the acid exists under the conditions employed in the form of the lactone.

---

c. Decarboxylation of substituted 8-methoxy-1-naphthoic acids.

As all attempts to decarboxylate 8-hydroxy-1-naphthoic acid led to the formation of the lactone, it was thought that success might be achieved by making use of the methoxy acid.

The method of methylation was first tried out with 8-hydroxy-1-naphthoic acid. Decarboxylation of the 8-methoxy acid would, however, yield α-methoxy-naphthalene, which is a liquid and not readily identified in small quantities. For this reason 5-nitro-8-methoxy-1-naphthoic acid, prepared directly from 5-nitro-8-bromo-naphthoic acid, was finally examined as this should lose carbon dioxide to form the solid compound, 4-nitro-1-methoxy-naphthalene.

(i) Preparation of 8-methoxy-1-naphthoic acid.

Ref:- Rule, Spence and Bretscher, J.C.S., 1928, 1500.

2 gms. 8-hydroxy-1-naphthoic acid

30 c.c. N/1 sodium hydroxide

7 gms. dimethyl sulphate.

The hydroxy-acid was dissolved in the sodium hydroxide. To the cooled solution the dimethyl sulphate was added with constant shaking over a period of half-an-hour, the product then being heated to 100° to destroy any excess of dimethyl sulphate.

Extraction with ether removed the methyl ester of the methoxy acid from the alkaline solution. On evaporating off the ether and recrystallising the product from petrol ether (b.p. 40-60°) the methyl-8-methoxy-1-naphthoate was obtained as colourless rhombic plates of melting point 50-52°.

Weight, 1 gm. representing 39% of the starting material.

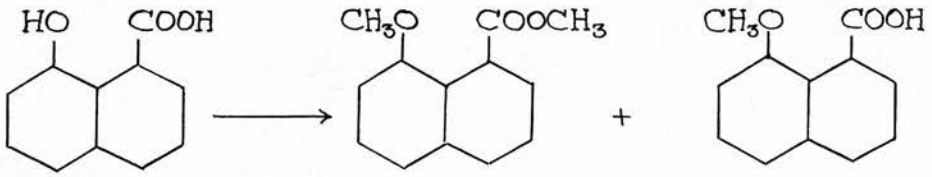
The alkaline aqueous layer contained the methoxy acid and a trace of unmethylated hydroxy acid. The latter was removed by adding diazotised sulphanilic acid which coupled in the alkaline solution with the hydroxy acid. After standing for 3 hours, the methoxy-acid and the dyestuff were precipitated with hydrochloric

acid as a viscous mass which soon solidified. This solid was filtered off and dried on a porous plate over phosphorus pentoxide.

The methoxy-acid was extracted with benzene, leaving the dye behind as a dark red powder.

From the benzene the methoxy acid separated as glistening needles of melting point 162-163°.

Weight, 1·2 gm. representing 50% of the starting material.

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Now if the substituted methoxy acids prepared by this method should correspond with those prepared from known substituted 8-bromo-1-naphthoic acids, there is no need for the decarboxylation of the methoxy acids. However, it is evident that this comparison has only limited application as it depends on whether or not the substituted bromo-acid corresponding to the substituted methoxy acid in question is known.

---

(ii) Preparation of 5-nitro-8-methoxy-1-naphthoic acid.

4 gms. 5-nitro-8-bromo-1-naphthoic acid

50 c.c. methyl alcohol

1 gm. sodium

0·5 gm. copper bronze.

Sodium methoxide was prepared by dissolving the sodium in the methyl alcohol. The acid was dissolved in this solution, the copper bronze added, and the product boiled under reflux on a water bath for one hour. After some time a yellow solid separated.

When cold, sufficient water was added to dissolve the yellow solid which was apparently a sodium salt. The copper was removed by filtration and the filtrate acidified with nitric acid, when a yellow precipitate formed. This precipitate was filtered off, washed with water and dried. It was recrystallised from 30 c.c. glacial acetic acid from which it separated as long narrow yellow rhombic prisms.

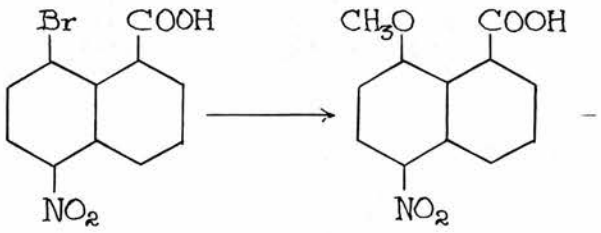
Yield, 2·7 gms.

The product melted at 252-3°; a mixture with the starting material (m.p. 245-247°) melted at 221-233°. It contained nitrogen, but no halogen, and was acidic.

Analysis. Nitrogen by Micro-Dumas Method.

| | |
|---|---|
| Calculated for 5-nitro-8-methoxy-1-naphthoic acid, | 5·7% |
| Found, | 5·7% |

The compound was therefore 5-nitro-8-methoxy-1-naphthoic acid, and the above yield represents 80% of the theoretical.




(iii) Decarboxylation of 5-nitro-8-methoxy-1-acid.

1 gm. 5-nitro-8-methoxy-1-naphthoic acid

2 c.c. dry quinoline

0·5 gm. copper bronze

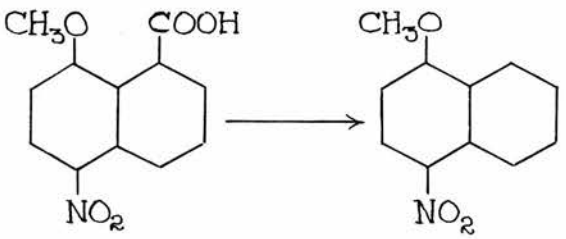
The decarboxylation was effected as in previous cases, the acid was dissolved in the boiling quinoline, the copper bronze carefully added, and the heating continued for 15 minutes after the addition of the copper.

When cold, the product was extracted with ether, which extract was washed successively with dilute hydrochloric acid, sodium carbonate and water. After drying over calcium chloride, the ether was removed by

evaporation, leaving a dark brown gummy residue. This residue was dissolved in boiling aqueous alcohol, from which, on cooling, yellow needles separated.

The product was non-acidic. It melted at 77-79°. Woroshzow (see Van der Kam's "Naphtalin Derivate") quotes 81° as the melting point of 1-methoxy-4-nitronaphthalene. As this product is not readily accessible for a mixed melting point, the source and the melting point of the above product were accepted as sufficient proof that it was 1-methoxy-4-nitronaphthalene.

As in all cases of decarboxylation carried out by the present writer, where the end-product was a solid of melting point below 100°, a relatively small yield was obtained. In the above case, 0·1 gm. of 1-methoxy-4-nitronaphthalene was obtained. This, however, was sufficient for identification purposes.

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This method which consists in methylating the substituted hydroxy acid (or lactone) and decarboxylating the resulting methoxy acid appears as if it would

be applicable to the problem under examination. However, while this work was in progress Goldstein and Francey (loc. cit.) recorded the orientation of the mono-substituted naphtholactones or hydroxy acids by preparing them from the corresponding mono-substituted naphthastyrils of known constitution, so this work was not carried further.

Owing to the difficulty of diazotising di-substituted naphthastyrils (see Section II C) Goldstein and Francey's method will probably not be applicable to the disubstituted hydroxy acids if and when they are prepared. In such cases it is probable that the above method may prove of value.

---

## II B. THE PREPARATION Of NAPHTHASTYRIL.

The methods previously used for the preparation of naphthastyril have been outlined in the Introduction to this thesis (p. 20). Unfortunately these methods involve several stages and only result in very small yields. It was thought that since 8-bromo-1-naphthoic acid is now readily obtainable in quantity, naphthastyril might be obtained directly from it owing to the reactivity of the bromine in the 8-position.

Many unsuccessful attempts were made to prepare

naphthastyril from 8-bromo-1-naphthoic acid before success was achieved. The work is traced in order in the following pages.

---

a. Preparation of naphthastyril from 8-bromo-1-naphthoic acid.

(1) By analogy with the preparation of 8-hydroxy-1-naphthoic acid from 8-bromo-1-naphthoic acid by boiling with sodium hydroxide solution in presence of copper bronze as catalyst, it was thought that naphthastyril might be prepared from the bromo-acid by fusing with sodamide.

The bromo-acid, together with excess sodamide and copper bronze were placed in a pyrex test-tube, and heated in an oil-bath. When the temperature reached about 100°, the mixture decomposed explosively, leaving only a black residue which was not further examined.

---

(2) The above experiment was repeated, using the sodium salt of the bromo-acid. However, when the temperature reached about 130°, the contents of the tube went black, and so were not further examined.

---

(3)

2 gms. 8-bromo-1-naphthoic acid

30 c.c. dekalin

0·7 gms. copper bronze.

The bromo-acid was suspended in the dekalin in a wide-necked 100 c.c. bolt-head flask. The flask was fitted with an inlet tube which passed below the surface of the dekalin, and also with a mercury-sealed mechanical stirrer and a reflux air condenser. The copper bronze was added, and ammonia gas, dried by passing through a soda-lime tower, passed through the dekalin suspension which was stirred. This was continued for 1 hour in the cold, and then the temperature was gradually raised on an oil-bath until the dekalin was boiling. The contents of the flask assumed a dark green colour. The heating was continued for 6 hours.

50 c.c. of water were added and the mixture boiled for 1 hour. If the reaction had occurred in the direction anticipated, the ammonium salt of the 8-amino-acid should go into solution in the water.

The dekalin was removed by steam distillation. The remaining solution was acidified with acetic acid and evaporated to smaller bulk. On cooling, white needle-shaped crystals appeared which were filtered off, washed with cold water and dried. After recrystallisation from absolute alcohol, the substance

melted at 159-160°.

Weight, 0·2 gms.

The product was an acid but contained neither halogen nor nitrogen.

A mixed melting point with α-naphthoic acid (m.p., 160°) gave no depression of the melting point, thus proving the product to be α-naphthoic acid.

---

(4) The above experiment was repeated but the temperature of the oil bath was maintained at 160-170° for 7 hours. The remainder of the experiment was carried out as in (3).

Yield, 0·3 gms. M.p., 159-160°.

The white needles obtained were again proved by a mixed melting point to be α-naphthoic acid.

The dark greenish-coloured residue left in the flask was then examined. It was boiled out with concentrated ammonium hydroxide and filtered. A dark bluish-green solution was obtained which on acidifying with acetic acid yielded a pale green precipitate. This was filtered off, and boiled with aqueous acetic acid, then filtered. The filtrate was made alkaline with sodium hydroxide and boiled, when a black precipitate of copper oxide was obtained. After filtering off the copper oxide, the filtrate was acidified with acetic acid, but no precipitate was obtained, and hence

no amino acid was present.

---

(5) On the assumption that the naphthoic acid was formed through the agency of the water liberated from the ammonium salt of the bromo-acid as it passed into the amide at higher temperatures, an attempt was next made to prepare naphthastyril from the acid amide of 8-bromo-1-naphthoic acid.

Preparation of 8-bromo-1-naphthamide.

Ref:- Rule and Barnett, J.C.S., 1932, 178.

5 gms. 8-bromo-1-naphthoic acid

15 gms. thionyl chloride.

The bromo-acid was dissolved in the thionyl chloride in a 100 c.c. round-bottomed flask fitted with a ground-in reflux condenser, and heated on a boiling water bath. After about 1 hour, the reaction was complete and sulphur dioxide ceased to be evolved. The excess thionyl chloride was then removed by distillation under reduced pressure on a boiling water-bath.

Excess solid ammonium carbonate was added and ground up with the acid chloride by means of a stirring rod. Carbon dioxide was evolved. The product was transferred to a filter by means of hot water, and washed several times with hot water. The solid was

dried and recrystallised from benzene. Crystals of melting point 179-180° were obtained, which were insoluble in sodium carbonate. They contained both halogen and nitrogen. A mixed melting point with 8-bromo-1-naphthoic acid (m.p. 179°) gave a depression of 44° (Rule and Barnett, loc. cit., record m.p. 179-180°).

Yield, 4 gms. representing 80% of the theoretical.

---

2 gms. 8-bromo-1-naphthamide

30 c.c. dekalin

0·7 gms. copper bronze.

The naphthamide was suspended in the dekalin in a wide-necked 100 c.c. bolt-head flask fitted with a reflux air condenser and a mercury sealed stirrer. The copper was added and the contents of the flask heated on an oil bath with stirring. The temperature of the bath was maintained at 150° for 3 hours. The copper only darkened very slightly, so the temperature was raised to about 200° and maintained there for a further five hours. The dekalin was removed by steam distillation, a black sticky substance being left with the water in the flask. The water was decanted off, and the residue shaken up with benzene and filtered. The benzene solution was boiled out twice with animal charcoal, filtered and dried with anhydrous sodium

sulphate. The benzene on removal by evaporation left a black sticky product. This product could not be purified from any solvent, so was not examined further.

---

(6) Groggins and Stirton (Ind. Eng. Chem., 1933, 25, 169) investigated the conversion of β-bromo-anthraquinone into β-amino-anthraquinone by treating it with ammonia under pressure in presence of different catalysts. They found the best catalyst to be a mixture of copper bronze, ammonium nitrate, and potassium chlorate.

This process was applied to the bromo-naphthoic acid.

1 gm. 8-bromo-1-naphthoic acid

10 c.c. 28% ammonium hydroxide (D = 0·902)

0·02 gms. copper bronze
0·25 gms. ammonium nitrate } ternary catalyst
0·02 gms. potassium chlorate

The bromo-acid, ammonium hydroxide, and the ternary catalyst were sealed together in a Carius tube. The bromo-acid went into solution as the ammonium salt, the solution being greenish tinged.

The tube was placed in a furnace, the temperature

raised to 160-180° over a period of 5 hours, and heating continued for 20 hours altogether.

When cold, the tube was opened. A yellowish-brown precipitate had formed. The contents of the tube were filtered and washed with a little cold water. The filtrate gave no precipitate on acidification with acetic acid.

The yellowish-brown solid was dissolved in the minimum amount of boiling water and filtered hot to remove the trace of copper. The filtrate, on cooling, deposited a crop of fine yellow needle-shaped crystals of melting point 180·5-181°.

Yield, 0·2 gms.

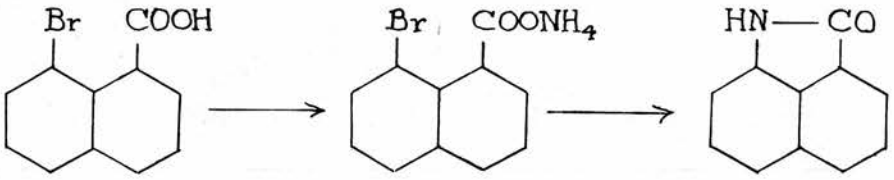
The substance contained no halogen (Beilstein's copper wire test) but contained nitrogen (sodium fusion). It was insoluble in sodium carbonate.

No depression was observed when a mixed melting point was taken with naphthastyril prepared by the reduction of 8-nitro-1-naphthoic acid by Ekstrand's method (loc. cit.). The substance was therefore proved to be naphthastyril.

The above quoted yield represents 30% of the theoretical.

It was found that naphthastyril prepared by reduction of 8-nitro-1-naphthoic acid was very difficult to purify, requiring several recrystallisations, whereas that prepared, as above, from the bromo-acid

required only one recrystallisation to bring it up to the correct melting point. Ekstrand quotes 180-181° as the melting point of naphthastyril.

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(7) The above experiment was repeated, but after the temperature of 160-180° had been reached, the heating was only continued for 1 hour.

On cooling and opening the tube, it was found that the precipitate was more crystalline than in the previous case. When filtered, it was yellow in colour.

It was recrystallised from boiling water as in (6), giving fine yellow needles of melting point 180·5-181°.

Yield, 0·35 gms. representing 52% of the theoretical.

The shorter period of heating thus increases the yield considerably.

---

(8) It was desired to find out whether or not the bromo-acid could be converted into naphthastyril by merely boiling with ammonia in presence of a catalyst.

A gramme of 8-bromo-1-naphthoic acid was dissolved in 50 c.c. concentrated ammonium hydroxide in a 100 c.c. bolt-head flask fitted with a reflux condenser. The same termary catalyst as used in experiments (6) and (7) was added. The solution was boiled for 2 hours and a further 10 c.c. of concentrated ammonium hydroxide was added, the heating being continued for another 2 hours.

The contents of the flask were allowed to cool, when a greenish-yellow crystalline solid separated. This was filtered off, washed with a little cold water, dissolved in 120 c.c. boiling water and filtered. On cooling, the naphthastyril separated in fine yellow needles.

Melting point, 181°, with sublimation.

Yield, 0·35 gms. representing 52% of the theoretical.

A repeat experiment gave 67% yield.

---

(9) Experiment (8) was repeated, but instead of using the ternary catalyst, 0·3 gms. of copper bronze

was used alone as catalyst.

1 gm. of 8-bromo-1-naphthoic acid yielded 0·30 gms. of naphthastyril, of melting point 181°C, representing a 45% yield.

A repeat experiment yielded 0·29 gms. of naphthastyril.

---

From experiments (8) and (9) it is evident that the aqueous ternary catalyst, consisting of 7% copper bronze, 7% potassium chlorate, and 86% ammonium nitrate is a better catalyst than copper bronze alone in the conversion of 8-bromo-1-naphthoic acid to naphthastyril.

The yields quoted above are practically the same whether the reaction was carried out in an open vessel or in a sealed tube.

---

The following work was carried out to transfer the reaction to a larger scale and also in an endeavour to increase the yield.

(10) 2 gms. 8-bromo-1-naphthoic acid

100 c.c. concentrated ammonium hydroxide.

{ 0·04 gms. copper bronze
  0·50 gms. ammonium nitrate
  0·04 gms. potassium chlorate. } ternary catalyst

The bromo-acid, ammonium hydroxide, and ternary catalyst were placed together in a small rotating autoclave. The autoclave was heated to 130-150° and maintained at that temperature for 1 hour. When cold, the autoclave was opened. Yellow crystals had deposited from the solution. The contents of the autoclave were filtered and the solid, which was much darkened by impurities, dissolved in 250 c.c. of boiling water. The solution was filtered; from the filtrate, on cooling, the naphthastyril crystallised out as fine yellow needles of melting point 181°.

Yield, 0·5 gms, representing 37% of the theoretical.

---

(11a) It was thought that perhaps the small yield in the above experiment might be due to the iron surface of the autoclave having a deleterious effect, so the experiment was repeated, using a glass lining in the autoclave.

2 gms. of 8-bromo-1-naphthoic acid yielded 0·94 gms. of naphthastyril of melting point 181°. This was further increased by evaporating to dryness the mother liquor from which the naphthastyril was recrystallised and recrystallising the residue from 10 c.c. of water. A further 0·04 gms. of naphthastyril was obtained.

Total yield, 0·98 gms.

The filtrate from the autoclave in this experiment was examined. It was found that on acidifying with acetic acid no precipitate formed, but on acidfying with hydrochloric acid a precipitate was obtained.

The filtrate was therefore acidified with hydrochloric acid, when a yellowish-brown precipitate was obtained. This precipitate was filtered off and boiled out with 30 c.c. of water and filtered. A dark brown residue was left on the filter paper. The filtrate, on cooling, deposited a crop of fine yellowish-coloured needles. These were found to contain halogen. When treated with cold sodium bicarbonate all but a very small amount, insufficient for a melting point, dissolved. The filtrate was again acidified, the precipitate filtered off and recrystallised from boiling water. The product obtained consisted of fine yellow needles. It contained halogen and was acidic; hence it was not naphthastyril - nor was it bromo-acid which always crystallises from water in colourless plates. It was however impure, melting at 150-160°, and was too small in quantity to examine further.

The total yield of naphthastyril from this experiment therefore represents 73% of the theoretical.

(11b) A repeat experiment in which the autoclave was maintained at 130-150° for 2 hours resulted in a 68% yield.

The most favourable conditions used up to this point were those obtaining in the first experiment carried out with the glass lining in the autoclave (11a).

---

(12) The reaction was then transferred to a much larger scale.

20 gms. 8-bromo-1-naphthoic acid

300 c.c. concentrated ammonium hydroxide

0·4 gms. copper bronze
5·0 gms. ammonium nitrate } ternary catalyst
0·4 gms. potassium chlorate

The bromo-acid, ammonium hydroxide, and catalyst were heated in the glass-lined autoclave at 130-150° for 1 hour as in experiment (11a).

The yellow crystalline solid was filtered off after cooling, washed with cold water, and recrystallised from 2·5 - 3 litres of water, giving 10 gms. of pure naphthastyril, m.p. 181°. An additional 1gm. was obtained by concentrating the mother liquor.

Total yield, 11 gms. representing 82% of the theoretical.

Repeat experiments gave the same yield.

---

Summary of conditions, yields, etc.

Naphthastyril from 8-Bromo-1-naphthoic acid.

| No. | Conditions | Catalyst | Temp. | Time of heating | % Yield | M.P. |
|---|---|---|---|---|---|---|
| 6 | Carius tube | Ternary | 160-180° | 20 hrs. | 30 | 180·5 -181° |
| 7 | " | " | " | 1 hr. | 52 | " |
| 8 | Open vessel | " | b.p. | 4 hrs. | av.60 | 181° |
| 9 | " | copper alone | " | " | av.45 | " |
| 10 | Autoclave (iron surface) | Ternary | 130-150° | 1 hr. | 37 | " |
| 11a | Autoclave (glass-lined) | " | " | " | 73 | " |
| 11b | " | " | " | 2 hrs. | 68 | " |
| 12 | " (large scale) | " | " | 1 hr. | 82 | " |

The above method for preparing naphthastyril (12) is a great improvement on the previous methods, as it involves fewer stages, is much simpler, and gives very much better yields.

b. Attempted preparation of naphthastyril from 8-hydroxy-1-naphthoic acid.

The reason for attempting this was that naphthylamines are obtained from the corresponding naphthols by treating with ammonia under pressure. In addition, the presence of a carboxyl group in position 1 is known to activate a halogen atom or a nitro group in position 8 (Rule and Barnett, J.C.S., 1932, 176). It was therefore considered of interest to examine whether the hydroxyl group in the peri-hydroxy-acid is labile.

(1) 1 gm. 8-hydroxy-1-naphthoic acid

50 c.c. concentrated ammonium hydroxide

0·3 gms. copper bronze

The hydroxy-acid was dissolved in the ammonium hydroxide in a 100 c.c. bolt-head flask fitted with a reflux condenser. The copper bronze was added and the solution boiled for 4 hours. Additions of ammonium hydroxide were made from time to time as the ammonia boiled off.

On cooling, no solid deposited as in the preparation of naphthastyril from the bromo-acid.

The solution was filtered to remove the copper. On acidifying with acetic acid no precipitate was obtained, but on acidifying with hydrochloric acid a red-brown gelatinous precipitate formed.

This precipitate could not be purified. There was no trace of naphthastyril.

---

(2) In which a smaller proportion of copper was used and a sealed tube employed.

0·5 gms. 8-hydroxy-1-naphthoic acid

6 c.c. 28% ammonium hydroxide

0·05 gms. copper bronze.

The hydroxy-acid, ammonium hydroxide, and copper were sealed together in a Carius tube. The tube was heated to 150-170°, taking the temperature up very slowly and maintaining it between those limits for 4 hours.

The contents of the tube had changed in colour from green to dark brown, but there was no precipitate.

The tube was opened and the contents filtered to remove the copper. On acidifying the filtrate with hydrochloric acid, a red-brown gelatinous precipitate was obtained as in the previous experiment.

The precipitate was not further examined, but there was no trace of naphthastyril.

---

Note:-

The above work on naphthastyril was completed during the early months of 1933 (February -March) and was communicated to the Department of Scientific and Industrial Research in a report dated September 1933. In the October issue of the British Chemical Abstracts (published in November) the abstract of a paper by Corbellini and Barbaro (Giorn. Chim. Ind. Appl., 1933, 15, 335-7) states that naphthastyril may be obtained from 8-bromo-1-naphthoic acid, but no further detail is given. Chemisches Zentralblatt (1933, II, 19, 2818 (Nov.)) gives a more detailed abstract. "Crude bromo-acid (m.p. 162-7°) was treated with 30% ammonia under pressure at 150° for 5 hours; yellow-green crystals of m.p. 175-178° were obtained, which after treating with sodium hydroxide and reprecipitating with hydrochloric acid were practically pure. Yield, 94%".

It will be observed that this method is practically the same as that adopted by the present writer, although it is not stated in the abstract that the Italian worker used copper bronze as catalyst. The method given in this thesis, however, has the decided advantage that it can be carried out in one-fifth of the time required for Corbellini's method.

## II C. THE DETERMINATION Of The CONSTITUTION Of CERTAIN DISUBSTITUTED NAPHTHASTYRILS.

The disubstituted naphthastyrils under consideration are the dibromo-, dichloro-, and dinitro-naphthastyrils prepared by Ekstrand (see Introduction, p. 23).

Owing to the difficulty of preparing these compounds in quantity, no attempts have been made by previous workers to determine their constitution. In fact, little or no reference appears to have been made to them in the literature since Ekstrand's paper was published in 1888 until the dichloro-derivative was obtained by Rule and Barnett (loc. cit.) by the action of thionyl chloride on 8-nitro-1-naphthoic acid.

Several attempts were made during the course of the present work to determine the constitution of the dichloro-derivative prepared from the 8-nitro-acid by heating it under pressure with fuming hydrochloric acid, but without success, probably owing to the small quantities available. However, since naphthastyril has now been shown (p. 89) to be obtainable in quantity from 8-bromo-1-naphthoic acid, and as these disubstituted derivatives can be obtained by direct substitution, they are now preparable in sufficient

quantity to allow much more extensive work to be carried out on the problem.

The work on the dichloro-compound is not given here, but the methods employed were essentially the same as those detailed below for the dibromo-derivative.

---

1. Preparation of Dibromo-naphthastyril.

Modified from Ekstrand (loc.cit.)

20 gms. naphthastyril

150 c.c. glacial acetic acid

1 gm. iodine

20 c.c. bromine.

The naphthastyril was dissolved in the acetic acid in a 500 c.c. bolt-head flask heated on a boiling water-bath. After the addition of the iodine, the bromine, dissolved in an equal volume of glacial acetic acid, was slowly added drop by drop with stirring. A vigorous reaction took place, fumes of hydrobromic acid were evolved, and a yellow precipitate formed almost immediately. The heating and stirring were continued for about 4 hours after the addition of the bromine, when the reaction seemed to be complete.

After standing overnight the product was filtered, washed with a little acetic acid, water, aqueous sodium

thiosulphate, and again water. The solid was boiled out with 1 litre of water to remove any unchanged naphthastyril, and filtered. Only a trace of naphthastyril separated from the filtrate on cooling.

The dibromo-naphthastyril was dried and recrystallised from about 1 litre of glacial acetic acid, from which it separated in golden-yellow needles of melting point 270-272°. Ekstrand quotes 268-270°.

Yield, 35 gms. representing 90% of the theoretical.

---

## 2. Determination of the Constitution of Dibromo-naphthastyril.

The method aimed at was the conversion of dibromo-naphthastyril into the corresponding tribromo-naphthoic acid, followed by the removal of halogen from position 8. In the first stage it was proposed to use a modified Sandmeyer reaction as employed by Goldstein and Francey (loc. cit.) for the preparation of 5:8-dibromo-1-naphthoic acid from 5-bromonaphthastyril. When naphthastyrils are dissolved in aqueous alkali, the anhydride ring is opened, yielding the sodium salts of the amino acids, which solutions can then be diazotised. This reaction was carried out with many variations in conditions in an endeavour to increase

the yield of end-product, the results being outlined in the following pages.

Naphthastyril has already been shown to brominate in the 5-position, so that it only remains to determine the position of the second bromine atom in dibromo-naphthastyril.

---

a. Attempted preparation of a tribromo-naphthoic acid from dibromo-naphthastyril.

(i) The dibromo-naphthastyril (5 gms.) was boiled for 4 hours with 4 gms. sodium hydroxide and 150 c.c. water. A dark brown solution was obtained, but on cooling, a precipitate formed. Under these conditions the naphthastyril would be present as the sodium salt of the amino acid; the precipitate was probably also the sodium salt which was apparently somewhat insoluble in water.

The diazotisation was attempted by adding 1·5 gms. sodium nitrite to the solution of the sodium salt and adding the whole at 0° over a period of half-an-hour to a mixture of 10 c.c. concentrated sulphuric acid and 20 c.c. of water with efficient mechanical stirring.

Cuprous bromide was prepared according to the method given in Vanino's "Präparative Chemie", Anorganische Teil, p. 495. Sulphur dioxide was passed

into a hot aqueous solution of 40 gms. copper sulphate and 33 gms. sodium bromide, when the cuprous bromide separated out as a white crystalline precipitate. It was filtered at the pump, washed with air-free water until no smell of sulphur dioxide remained, and dried by suction for a few minutes. The cuprous bromide was suspended in a mixture of 22c.c. concentrated sulphuric acid and 40 c.c. water in a beaker and cooled to 0°.

The diazo solution was run into this suspension with stirring and cooling at such a rate that the temperature did not rise above 5° (1 hour). Although there was frothing there was no vigorous evolution of nitrogen. After standing overnight at room temperature, the product was heated on a water-bath to 80° and maintained at that temperature until all frothing had ceased. On cooling, the dark brown solid was filtered off and washed with water.

The solid was boiled out with aqueous sodium carbonate and filtered. On acidification with hydrochloric acid, the filtrate precipitated a dark brown solid which, after standing for some time, was filtered off and washed with water. It was boiled out with animal charcoal in aqueous alcohol (1:1) from which, on cooling, a brown solid separated which, however, was still impure, melting over a range from 190 to 215°.

Recrystallisation from benzene and twice from acetic acid gave colourless needles melting at 251-252°. Further crystallisation did not affect the melting point. The product was now a pale buff colour. It was acidic and contained bromine but no nitrogen.

The yield was very small - about 0·2 gms.

Analysis. Bromine by Carius method.

| | |
|---|---|
| Found, | 48·5% |
| Calculated for tribromo-naphthoic acid, | 58·7% |
| " " dibromo-naphthoic acid, | 48·5%. |

A repeat analysis gave the same result.

The acid obtained was therefore a dibromo-naphthoic acid and not a tribromo acid as was expected. Evidently the diazo group had been replaced by hydrogen instead of bromine, thus resulting in a dibromo-acid.

The alkali insoluble portion, which was dark brown in colour, was repeatedly boiled out with glacial acetic acid until the residue proved to be completely inorganic. On pouring the acetic acid extract into a large volume of water a yellow precipitate formed, which was filtered off, washed with water and recrystallised from glacial acetic acid. Yellow needles were obtained which melted at 270-272°. A mixed melting point with dibromo-naphthastyril proved that the product was unchanged starting material. Weight, 3 gms.

The pale grey inorganic residue was probably cuprous bromide. It contained copper and bromine, was insoluble in water, but dissolved in ammonium hydroxide with the production of a deep blue colour.

Since the dibromo-naphthastyril was only extracted from the alkali insoluble portion by continued boiling with acetic acid, it is probable that the dibromo-naphthastyril and cuprous bromide had formed some type of complex.

The yield of dibromo-acid thus obtained, allowing for recovered starting material, is 10% of the theoretical.

---

The following experiments were carried out in an attempt to prepare the tribromo-acid instead of the dibromo-acid. As the methods are similar to that already described, they are only given briefly.

(ii) As was observed by Ekstrand, it was found that dibromo-naphthastyril only dissolved with great difficulty in alkali. A large excess of alkali and a large volume of water had to be used to obtain a solution of the sodium salt of the amino acid.

The dibromo-naphthastyril (5 gms.) was dissolved by boiling for 4 hours with 6 gms. sodium hydroxide and 400 c.c. water.

The diazotisation was effected by adding 1·5 gms. sodium nitrite, as in the previous experiment, and adding slowly, with cooling and stirring, to 20 c.c. concentrated sulphuric acid.

This solution was added to/a suspension of cuprous bromide in 25 c.c. concentrated sulphuric acid and 25 c.c. water.

After completing the reaction as in (i), the brown solid obtained by acidifying the sodium carbonate extract was extracted with 250 c.c. benzene in a Soxhlet apparatus. The benzene was removed by evaporation, and the resulting solid boiled out with 20 c.c. glacial acetic acid and animal charcoal, and filtered. From the filtrate, on cooling, colourless needles crystallised out, which in bulk were buff-coloured. The melting point was from 248 to 250°, but a second recrystallisation gave 251-252°.

Yield, 0·3 gms.

As in the previous case, approximately 3 gms. of dibromo-naphthastyril were recovered from the alkali insoluble portion, so the yield of dibromo-acid obtained is 15% of the theoretical.

(iii) This experiment was a repeat of (ii), using 15 c.c. concentrated sulphuric acid and 15 c.c. water in the diazotisation, and suspending the cuprous bromide in 50 c.c. concentrated sulphuric acid and 25 c.c. water.

Again a small yield was obtained - 0·2 gms. of melting point 251-252°. Approximately 3 gms. of the starting material were recovered as in the previous cases.

Since only the dibromo-acid was obtained, the portion insoluble in benzene was examined to see if it contained the tribromo-acid.

This portion was dissolved in glacial acetic acid and boiled out with animal charcoal. On filtering and cooling, a yellow crystalline solid separated which was recrystallised again from glacial acetic acid. It was obtained as fine colourless needles which were yellow in bulk. The product, however, was still impure, melting with decomposition from 160-170°, and was too small in amount to purify further.

---

(iv) Experiment (iii) was repeated, the only variation being that the cuprous bromide was dissolved in a mixture of 25 c.c. concentrated sulphuric acid, 25 c.c. water, and 120 c.c. 35% hydrobromic acid.

The extraction was carried out with sodium

hydroxide instead of carbonate, whereby on acidification a more granular precipitate was obtained than previously, which was much more easily filtered than the gelatinous precipitate obtained from the sodium carbonate extract.

Yield of dibromo-acid, 0·1 gm. melting at 251-252°.

The fraction insoluble in benzene could not be purified.

---

(v) The diazotisation was carried out as in previous experiments, but the diazo solution was run into a boiling solution of cuprous bromide in 75 c.c. of 35% hydrobromic acid.

Yield of dibromo-acid, 0·12 gm. of melting point 251-2°, 3 gms. of starting material being recovered.

---

It is not readily understood why the diazo group should be replaced by hydrogen instead of halogen under the conditions employed. However, the smallness of the yield may be partly accounted for by the fact that dibromo-naphthastyril is difficult to diazotise. There are two reasons for this difficulty. Firstly, it is only in alkaline solution that the anhydride ring is open, the compound being then present as the sodium salt of the amino acid. On treatment with

acid, the naphthastyril is regenerated, so that in an attempt to effect the diazotisation probably the naphthastyril is formed before diazotisation takes place, as is supported by the fact that about 60% of the dibromo-naphthastyril was recovered in each of the above cases. Secondly, owing to the presence of the two bromine atoms the amino group in the dibromo-amino-acid is very weakly basic and is accordingly difficult to diazotise.

Hodgson and Walker (J.C.S., 1933, 1620) have described a method for the diazotisation of weakly basic amines such as 2:4-dinitro-1-naphthylamine, and this method was applied to the problem in hand.

Further, since in the above experiments the diazo group was replaced by hydrogen, conditions more suitable for the replacement of the diazo group by hydrogen were employed in an endeavour to increase the yield of dibromo-acid.

---

(vi) A solution of the sodium salt was prepared by dissolving 5 gms. dibromo-naphthastyril in sodium hydroxide as in experiment 2. The solvent was then removed as completely as possible by evaporation.

Sodium nitrite, 3 gms. was added to 40 c.c. of cooled concentrated sulphuric acid with stirring. The temperature was raised to 70° until the nitrite

dissolved, and the solution was then cooled to room temperature. Sodium bisulphate precipitated but was not filtered off.

The sodium salt of the amino-acid prepared above was gradually added, with stirring, to the nitrite solution, the temperature being kept below 20°. An equal volume of glacial acetic acid (60 c.c.) was added, and the whole poured into 100 c.c. ethyl alcohol. The temperature was gradually raised to 80° and maintained at that temperature until all frothing had ceased.

A yellow precipitate deposited, which was filtered off and recrystallised from glacial acetic acid, from which it separated in yellow needles, similar to dibromonaphthastyril. A melting point and mixed melting point proved it to be unchanged dibromo-naphthastyril. Weight, 3 gms.

The filtrate from the diazotisation was steam-distilled to remove alcohol, acetic acid, and ethyl acetate which had formed. However, extensive decomposition took place at this stage, so that no further product could be isolated.

It is difficult to account for the complete failure in this case to separate any dibromo-acid, but it is possible that the supposed sodium salt of the amino acid was in reality dibromo-naphthastyril, so

that no diazotisation actually took place. Ekstrand did not obtain the sodium salt of this compound. He states that the preparation of it presents great difficulty, so that on evaporating the alkaline solution, dibromo-naphthastyril and sodium hydroxide are probably the main end-products.

---

If the tribromo-acid had been obtained, it was purposed removing the halogen from the 8-position, and decarboxylating the resulting dibromo-acid to obtain a dibromo-naphthalene which could probably be identified, because all the possible isomeric dibromo-naphthalenes are known, with the exception of the 2:3-derivative. However, since the dibromo-acid was obtained, and not the tribromo-acid, the dehalogenation stage is unnecessary.

---

b. <u>Decarboxylation of the above dibromo-naphthoic acid.</u>

0·5 gms. dibromo-naphthoic acid

0·25 gms. copper bronze

1 c.c. quinoline

The decarboxylation was effected in the usual way by boiling the acid in quinoline in presence of copper bronze for half-an-hour (see p. 43).

When cold, the contents of the flask were extracted with ether. A yellow-coloured solid was left undissolved, but could not be identified.

The ether extract was washed with dilute hydrochloric acid, aqueous sodium carbonate, and finally water. On removing the ether by evaporation, a dark reddish-brown gummy substance was obtained, which was dissolved in acetone and boiled out with animal charcoal. The acetone was removed under reduced pressure at room temperature, the solid which was left being much lighter in colour and less sticky. It was extracted with petrol ether (b.p. 40-60°) which dissolved all but a small fraction of the substance.

During the evaporation of the solvent, long colourless needles appeared, and eventually a pale yellow solid was obtained.

The weight was very small, being 0·02 gm., which is only about 10% of the usual yield, and too little to allow further purification. It was, however, comparatively pure, melting over a range of two degrees at 56-58°. The melt, on solidifying, remelted at the same temperature.

The product was non-acidic and was presumably a dibromo-naphthalene.

---

The melting point of the product eliminates all the dibromo-naphthalenes except the 1:2, the 1:3, and the 1:6 isomers, melting points 68°, 64° and 61° respectively (Van der Kam, "Naphtalin Derivate").

From a consideration of the starting material there are two possibilities. As previously stated, naphthastyril brominates first in the 5-position. The second bromine atom possibly enters either position 4 or position 7, the latter being highly probable in view of the strong activation of this position by the imino group. Accordingly, the dibromo-acid obtained above will probably be either 4:5-dibromo-1-naphthoic acid or 5:7-dibromo-1-naphthoic acid, neither of which is described in the literature. The dibromo-naphthalene obtained by the decarboxylation of the dibromo-acid will, on this assumption, be either the 1:8 or the 1:3 isomer. 1:8-Dibromo-naphthalene melts at 109° ( Van der Kam ) , whereas the 1:3 isomer melts at 64°, so that the melting point of the product obtained above eliminates the former and indicates the latter.

To test this conclusion, 1:3-dibromo-naphthalene was prepared from another source.

---

c. Preparation of 1:3-dibromo-naphthalene.

Meldola (Ber., 1879, 12, 1961) prepared this

compound from 2:4-dibromo-1-naphthylamine. The reaction, however, was not found to proceed smoothly. Meldola brominated N-acetyl-α-naphthylamine in the cold (Ber., 1878, 11, 1906) obtaining N-acetyl-4-bromo-1-naphthylamine which he further brominated by allowing to stand in presence of bromine at room temperature for a fortnight. The dibromo compound thus obtained on hydrolysis yielded 2:4-dibromo-1-naphthylamine which, on diazotisation and boiling with alcohol, yielded 1:3-dibromo-naphthalene.

It was not practicable to carry out Meldola's preparation as he did it, owing to the time involved; the dibromination of acetyl-α-naphthylamine was therefore attempted in boiling glacial acetic acid solution. A tarry substance was obtained, from which was isolated several grams of the mono-bromo derivative, but only a fraction of a gram of the dibromo-product. The yield quoted by Meldola was also small.

Another method for preparing 2:4-dibromo-1-naphthylamine was therefore sought. This was found in the work of Franzen and Aaslund (J. pr., 1917, 95, 165).

---

(1) Preparation of Benzylidene-1-naphthylamine.

15·5 gms. α-naphthylamine

11·5 gms. benzaldehyde.

The α-naphthylamine and benzaldehyde (equimolecular

quantities) were heated together on a boiling water-bath for 1 hour. The solution, on standing overnight in the refrigerator, went completely solid. The product was recrystallised from 50 c.c. alcohol, from which the benzylidene-1-naphthylamine separated in yellow plates of melting point 73°.

Yield, 21 gms. representing 84% of the theoretical.

---

(ii) Preparation of 2:4-Dibromo-1-naphthylamine.

Ref.:- Franzen and Aaslund, loc. cit.

The benzylidene-1-naphthylamine (21 gms.) was dissolved in 65 c.c. chloroform. This solution was cooled in ice and 15 gms. bromine dissolved in 10 c.c. chloroform slowly added with stirring, so that the temperature did not rise above 30°.

The thick yellow mass, after standing for 2 hours, was treated with 7·5 gms. pyridine, and to the dark solution thus obtained another 15 gms. bromine dissolved in 10 c.c. chloroform were added. After standing for a further 2 hours, 30 c.c. absolute alcohol were added and the whole boiled under reflux for 1 hour.

On cooling, a precipitate appeared which was filtered off, and the filtrate steam-distilled until no more chloroform and alcohol distilled over. A dark solid separated, which was dissolved in boiling

alcohol, and boiled with animal charcoal. The solution was poured into a large volume of water, when a grey solid separated. This was filtered off, washed with water and dried.

The two solid products obtained were put together (weight, 15 gms.) and repeatedly recrystallised from aqueous alcohol, from which the dibromo-naphthylamine eventually separated in pale yellow needles of melting point 115-118° (Meldola quotes 118-119° - the above authors, 113-115°).

Yield, 4·8 gms.

---

(iii) Preparation of 1:3-dibromo-naphthalene.

The diazotisation of the above dibromo-naphthylamine was carried out by the method already mentioned (p. 104) (Hodgson and Walker, loc. cit.).

Sodium nitrite (1·5 gms.) was added to 15 c.c. cooled concentrated sulphuric acid, with stirring. The temperature was raised to 70° until the nitrite dissolved. On cooling, sodium bisulphate separated but was not filtered off.

The dibromo-naphthylamine (4·8 gms.) was dissolved in 60 c.c. glacial acetic acid and added gradually, with stirring, to the cooled nitrite solution.

An equal volume of ethyl alcohol (80 c.c.) was

added, with cooling, to the diazo solution and the temperature gradually raised to 80° until all frothing had ceased.

The mixture was next steam-distilled, when ethyl alcohol and acetate distilled over first. On further distillation, the dibromo-naphthalene came over as an oil which solidified to a white solid. It was re-crystallised from alcohol, from which it separated as colourless needles of melting point 64°.

Yield, 2 gms., representing 44% of the theoretical.

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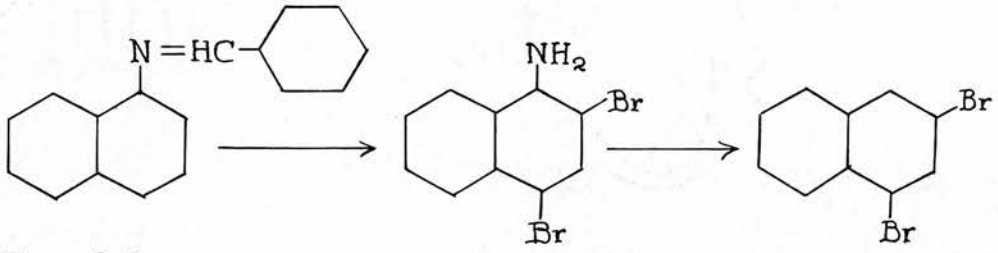


Benzylidene-1-naphthylamine → 2:4-Dibromo-1-naphthylamine → 1:3-Dibromo-naphthalene

---

A mixed melting point was then taken with the above 1:3-dibromo-naphthalene and the dibromo-naphthalene obtained from dibromo-naphthastyril.

| | |
|---|---|
| Melting point of 1:3-dibromo-naphthalene, | 64° |
| " " " dibromo-naphthalene from dibromo-naphthastyril, | 56-58° |
| " " " mixture, | 57-60° |

No depression of the melting point was observed; it was therefore concluded that the dibromo-naphthalene obtained from dibromo-naphthastyril is the 1:3 isomer. Accordingly, the dibromo-acid must be 5:7-dibromo-1-naphthoic acid (a new compound), and the dibromo-naphthastyril must have the bromine atoms in the 5 and 7 positions.

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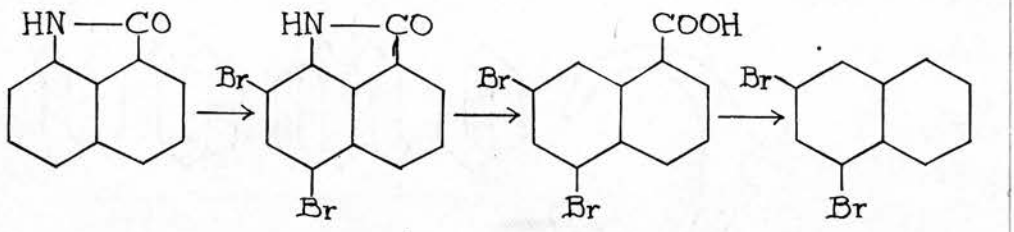
**Summary.**




Naphthastyril | 5:7-Dibromo-naphthastyril | 5:7-Dibromo-1-naphthoic Acid | 1:3-Dibromo-naphthalene

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Since Ekstrand's dichloronaphthastyril (m.p.,264-265°) was prepared by methods similar to those for preparing the dibromo-derivative, it is obvious that the dichloro compound will have the same structure, that is, 5:7-dichloro-naphthastyril. Ekstrand obtained a dinitro-naphthastyril (m.p.,above 290°) directly from the above dibromo compound by treatment with fuming nitric acid; this must therefore be

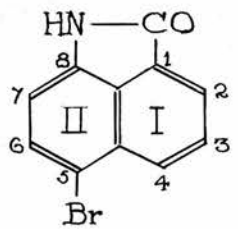
5:7-dinitro-naphthastyril.

---

Discussion.

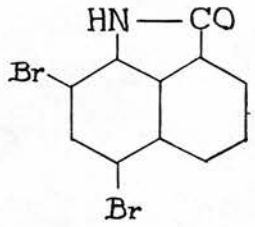
A salient feature in the interaction of bromine and naphthastyril is the ease with which the reaction takes place to produce an excellent yield of the dibromo-derivative. This is in keeping with the general experience (cf. also Francis, Chem. Reviews, 1926-7, 3, 279) that the amino group exerts an accelerative influence on further substitution.

On monosubstitution, the 5-position is the first to be attacked, partly owing to the ortho and para directive and activating influence of the imino group, and partly to the residual partial valence which is characteristic of the α-positions.




On further substitution there are apparently two competitive effects at work. Although the conjugated system in ring I is deactivated by the carboxyl group, which tends to retard further substitution in this ring, there is still the partial valence at position-4 to be considered. The presence

of the imino group and the bromine atom in ring II may be expected to lead respectively to an activation and a deactivation of this ring. It is therefore difficult to forecast on theoretical grounds whether the 4 or 7 position will be the more easily attacked. Experimental evidence shows that it is the 7-position almost exclusively, since the pure dibromo-derivative can be isolated in 90% yield.




Lack of sufficient data, however, makes any conjectures as to the influences at work in naphthalene derivatives highly speculative.

The above formula for dichloro-naphthastyril (p. 113) is the same as that tentatively advanced for it by Rule and Barnett (loc. cit.) from theoretical considerations.

## III A. SYNTHESIS Of NITRO-BROMO-NAPHTHOIC ACIDS From ACENAPHTHENEQUINONE.

### 1. 4-Nitro-8-Bromo-1-Naphthoic acid.

a. Preparation of 5-nitro-acenaphthenequinone.

Refs:- Rowe and Davies, J.C.S., 1920, 117, 1349.

Mayer and Kaufmann, Ber., 1920, 53, 296.

20 gms. acenaphthenequinone

100 c.c. concentrated sulphuric acid

15 c.c. nitrating mixture (5 c.c. fuming nitric acid and 10 c.c. concentrated sulphuric acid).

The nitrating mixture was prepared by mixing one molecular proportion of fuming nitric acid (D = 1·51) per mole of acenaphthenequinone with twice its volume of concentrated sulphuric acid.

The acenaphthenequinone was dissolved in the concentrated sulphuric acid in a 500 c.c. bolt-head flask. The flask was placed in an ice-bath and the nitrating mixture slowly added with constant shaking. At the end of the addition the mixture was warmed on a water-bath at 30° for 1 hour, and then poured on ice. After

standing overnight, it was filtered.

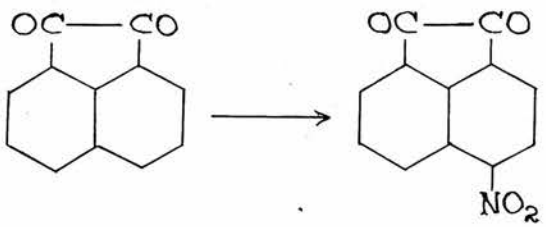
The above workers found that purification by immediate crystallisation was unsatisfactory, and that the best results were obtained by mild oxidation, which removed the impurities without affecting the nitro-quinone.

The product was dissolved in 500 c.c. glacial acetic acid, the solution was filtered and 10 gms. powdered sodium dichromate were added slowly to the filtrate. The mixture was heated on a boiling water-bath for quarter-of-an-hour and poured into water. A yellow solid separated which was left overnight, then filtered and dried.

Yield, 17 gms. of melting point 180-190°.

Repeated crystallisation from glacial acetic acid gave yellow needles of melting point 218°.

Yield, 10 gms., representing 40% of the theoretical.



b. Oxidation of 5-nitro-acenaphthenequinone to 4-nitro-naphthalic acid.

Ref. - Mayer and Kaufmann, loc. cit.

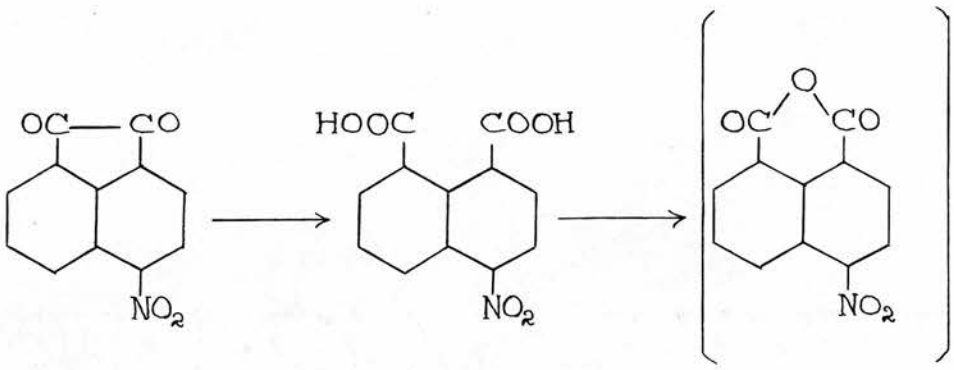
15 gms. 5-nitro-acenaphthenequinone
150 c.c. glacial acetic acid
10 gms. sodium bichromate.

The nitro-quinone was dissolved in the acetic acid in a 500 c.c. bolt-head flask by heating to 80° on a water-bath. Powdered sodium bichromate was slowly added, the temperature being kept below 85°. The solution was heated on a boiling water-bath for three hours and poured into water, when a yellow solid separated. This was allowed to stand overnight and was then filtered.

The product was dissolved in sodium carbonate and filtered to remove neutral impurity. The filtrate was acidified with nitric acid, when the nitro-naphthalic acid was reprecipitated. It was filtered, washed with water and dried. The acid was recrystallised several times from glacial acetic acid.

Yield, 12 gms., representing 70% of the theoretical.

Melting point as the anhydride, 220°C.

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c. Mercuration of 4-nitro-naphthalic acid.

Ref. - Leuck, Perkins and Whitmore, J.A.C.S., 1929, 51, 1831.

10 gms. 4-nitro-naphthalic acid

3·5 gms. sodium hydroxide

9 gms. yellow mercuric oxide

The nitro-naphthalic acid was dissolved in 200 c.c. water containing the sodium hydroxide, which was in slight excess of the calculated quantity. The mercuric oxide was dissolved in 10 c.c. glacial acetic acid and 30 c.c. water, giving a solution of mercuric acetate (1 mole of mercuric oxide per mole of nitro-naphthalic acid).

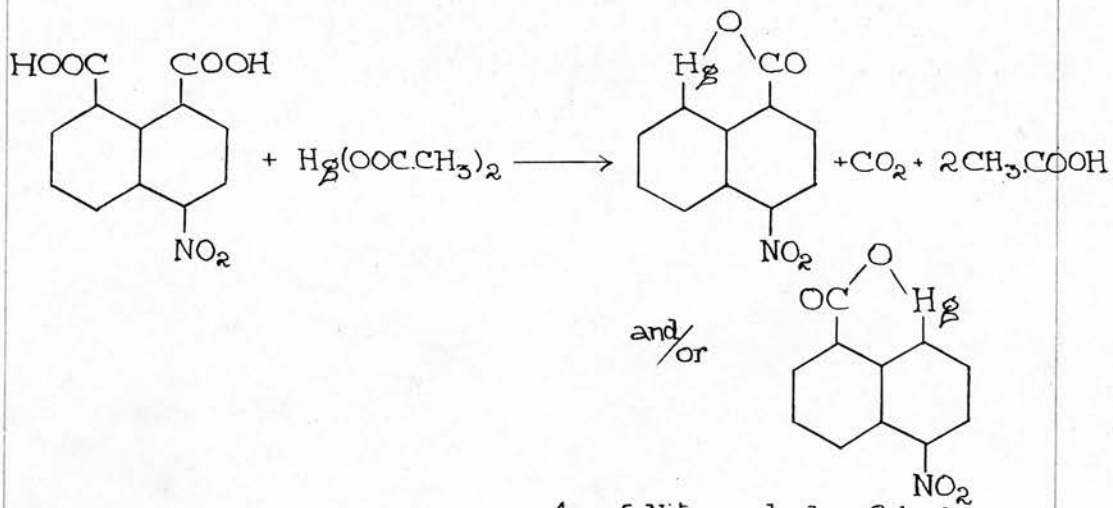
The two solutions were mixed in a 500 c.c. pyrex bolt-head flask and made distinctly acid with glacial acetic acid, when a yellow suspension formed.

The mixture was refluxed for 100 hours until all

carbon dioxide evolution had ceased. A test portion deposited no metallic mercury on a clean copper wire. The solid was only difficultly soluble in sodium hydroxide.

The product was filtered, washed with water, alcohol, and ether, and dried in a steam oven. It was a greyish-yellow powder.

Yield, 15 gms., representing 95% of the theoretical.




4 and 5-Nitro-anhydro-8-hydroxy-mercuri-1-naphthoic Acids.

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d. Bromination of the above mercuration product.

15 gms. mercuration product

5·8 gms. bromine

The mercuration product was suspended in 150 c.c. glacial acetic acid in a 500 c.c. beaker which was placed in an ice-bath and fitted with a mechanical

stirrer. The bromine was dissolved in 40 c.c. of a concentrated sodium bromide solution. This solution was added very slowly, over a period of one hour, with constant stirring, to the suspension of the mercuration product.

After the addition of the bromine solution, the product was heated to about 90° and maintained at that temperature for about quarter-of-an-hour, a yellowish-brown solution being obtained. This solution was poured into 500 c.c. of cold water, with stirring. A yellowish-brown precipitate formed which, after standing overnight, was filtered off, washed with cold water and dried.

Yield, 6 gms. M.p., 130-170°.

The product was dissolved in boiling acetic acid and boiled out several times with animal charcoal. On cooling, yellow crystals appeared, which however melted over a range. Repeated recrystallisation gave a product melting at 201-203°, but greatly diminished the yield.

Yield, 0·5 gms.

Analysis. Nitrogen (Micro-Dumas).

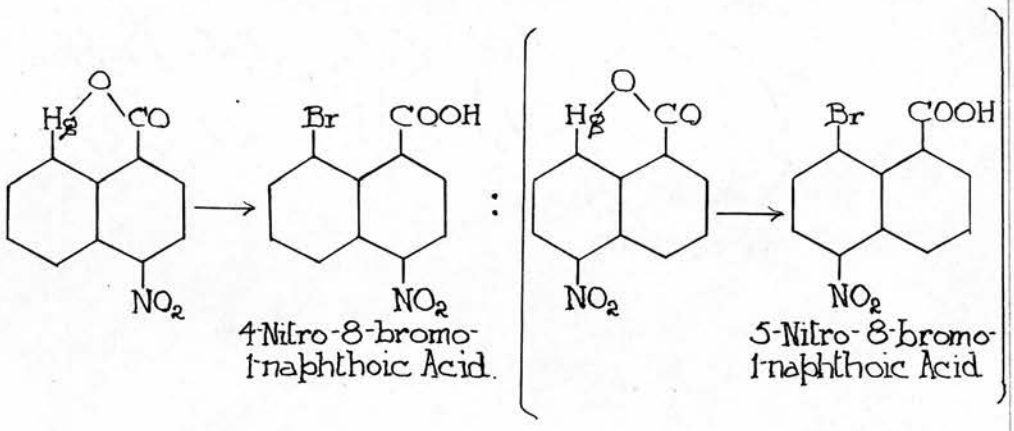
Calculated for X-nitro-8-bromo-1-naphthoic acid, 4·7%.

Found, 4·7%.

The compound obtained is therefore a mononitro-8-bromo-1-naphthoic acid. It can only be one of two isomers, namely, the 4-nitro or 5-nitro, since it was

obtained from 4-nitro-naphthalic acid. A mixture of the above acid and 5-nitro-8-bromo-1-naphthoic acid (m.p. 247°) melted several degrees below 200°, the acid obtained is therefore 4-nitro-8-bromo-1-naphthoic acid. It is readily soluble in alcohol, acetic acid and acetone, but less soluble in benzene and ether.

The small yield is probably due to the fact that a mixture of both 4- and 5-nitro-acids was produced, the yield being much diminished in the separation. Owing to the small quantities of material none of the 5-nitro-acid was isolated.

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Leuck, Perkins and Whitmore (loc. cit.) carried out the above mercuration, and by boiling the mercuration product with hydrochloric acid obtained 4-nitro-1-naphthoic acid and only a very small amount of the 5-nitro-acid. They state that with 4-nitro-naphthalic acid the replacement of the carboxyl group by mercury takes place almost entirely in the 8-position. The

quantities they worked with were very much larger than those employed above.

Owing to the limited time at my disposal the above preparation could not be repeated but, considering the yield of 4-nitro-1-naphthoic acid obtained by the above workers, it is probable that the yield quoted above for 4-nitro-8-bromo-1-naphthoic acid could be considerably increased.

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## 2. 4:5-Dinitro-8-bromo-1-naphthoic Acid, and 4:5-Dinitro-1-naphthoic Acid.

### a. Preparation of 5:6-Dinitroacenaphthenequinone.

Refs.- Rowe and Davies, J.C.S., 1920, 117, 1344.

Mayer and Kaufmann, Ber., 1920, 53, 289.

10 gms. acenaphthenequinone

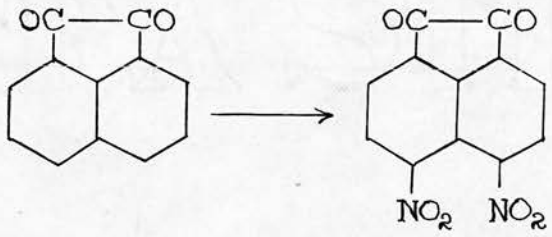
150 c.c. concentrated sulphuric acid

27 c.c. nitration mixture

The acenaphthenequinone was dissolved in the sulphuric acid, the solution being cooled in an ice-bath.

The nitration mixture, which was prepared by mixing 7 c.c. fuming nitric acid (D, 1·51) with 20 c.c. concentrated sulphuric acid, was slowly added, with constant shaking, to the cooled solution of acenaphthenequinone. When all the nitration mixture was added the product was warmed to 80° on a water-bath for one hour. After cooling, the solution was poured on ice, when a yellow precipitate formed, which after standing overnight was filtered off. The solid was washed thoroughly with dilute sodium carbonate and finally with water. It was dried and recrystallised from 200-250 c.c. concentrated nitric acid, from which it was obtained as orange-yellow needles of melting point 323° (decomp.).

Yield, 7·2 gms., representing 50% of the theoretical.

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b. Oxidation of 5:6-dinitroacenaphthenequinone to 4:5-dinitro-naphthalic acid.

Ref.- Mayer and Kaufmann, Ber., 1920, 53, 289.

10 gms. 5:6-dinitroacenaphthenequinone

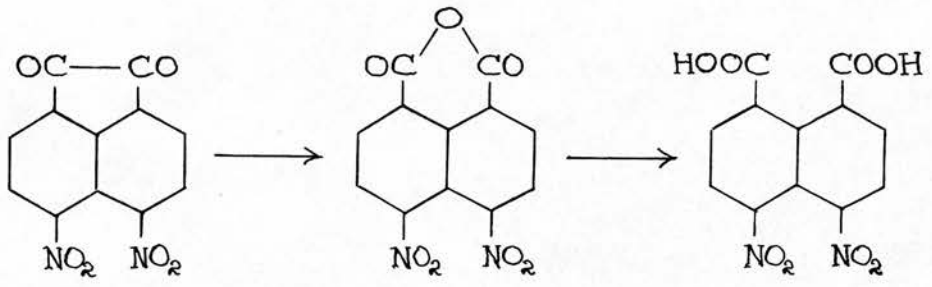
12·5 gms. powdered sodium bichromate.

The dinitroacenaphthenequinone was dissolved in 1 litre of boiling glacial acetic acid. After removing the bunsen from beneath the oil-bath on which the solution was being heated, the sodium bichromate was added.

The solution was boiled under reflux for 1 hour and then poured into a large volume of water. A yellow solid separated which, after standing overnight, was filtered off. It was dissolved in sodium carbonate, filtered to remove neutral impurity, and acidified with nitric acid. Almost pure dinitro-naphthalic acid was reprecipitated, which was used without further purification. The compound was yellow in colour.

Yield, 10·5 gms., representing 94% of the theoretical.

Melting point above 310°.



c. Mercuration of 4:5-dinitro-naphthalic acid.

10 gms. 4:5-dinitro-naphthalic acid

3 gms. sodium hydroxide

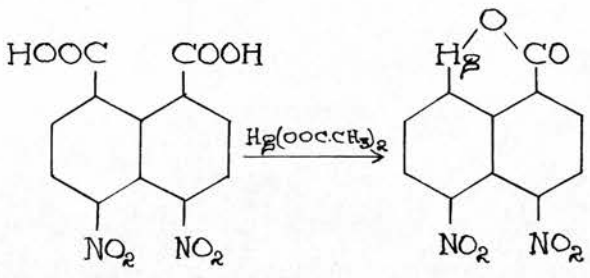
7·6 gms. yellow mercuric oxide.

The dinitro-naphthalic acid was dissolved in a solution of the sodium hydroxide in 200 c.c. water, with heating. A solution of mercuric acetate was prepared by heating the mercuric oxide with a mixture of 30 c.c. water and 10 c.c. glacial acetic acid.

These two solutions were mixed together in a 500 c.c. pyrex bolt-head flask, and the mixture made distinctly acid with glacial acetic acid, when a yellow-coloured suspension formed.

The whole was refluxed for 100 hours until a test portion deposited no metallic mercury on a clean copper wire. While boiling, the contents of the flask "bumped" vigorously and became dark brown in colour. When cold the product was filtered, washed with water, alcohol and ether, and dried at 100°.

Yield, 11 gms., representing 75% of the theoretical.




4:5-Dinitro-anhydro-8-hydroxy-mercuri-1-naphthoic Acid.

d. Preparation of 4:5-dinitro-8-bromo-1-naphthoic acid by the bromination of the above mercuration product.

11 gms. mercuration product

4 gms. bromine

To a cooled suspension of the mercuration product in 150 c.c. glacial acetic acid the bromine, dissolved in 30 c.c. of a concentrated solution of sodium bromide, was slowly added, with stirring, over a period of 1 hour.

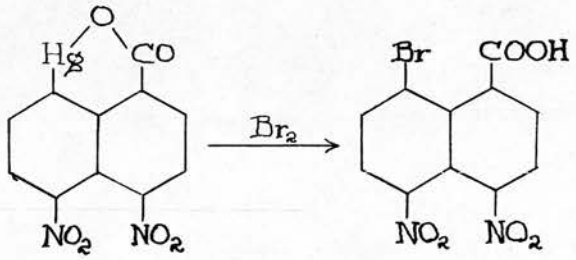
After the addition of the bromine solution, the mixture was heated to 90° and maintained at that for quarter-of-an-hour, when a dark brown solution was obtained. This solution was poured into 300 c.c. of cold water, with stirring; a dark brown solid separated, which after standing overnight was filtered off, washed with water and dried.

The solid was boiled out with animal charcoal in glacial acetic acid, from which it separated in yellow crystals. These were recrystallised from concentrated nitric acid, from which the compound was again obtained as yellow crystals.

Yield, 2·0 gms. Melting point, 248-252° with decomposition.

In this case only one possible dinitro bromo acid

can be produced from the dinitroacenaphthenequinone used as starting material, namely, 4:5-dinitro-8-bromo-1-naphthoic acid.




A mixture of this acid and 4:5-dinitro-8-bromo-1-naphthoic acid (m.p. 248-252°), prepared as on p. 33, melted unchanged at 248-252°.

The yield quoted above is 27% of the theoretical.

---

This result confirms the structure assigned by Mayer and Kaufmann (loc. cit.) to the dinitroacenaphthenequinone which was employed as starting material in this series of preparations. The proof advanced by these authors lay in a comparison of the melting points of the dinitro-naphthalic anhydrides prepared respectively from 5:6-dinitro-acenaphthene and from dinitroacenaphthenequinone. The anhydrides were found to melt unsharply at about 310°, and the proof of their identity was apparently not regarded as entirely conclusive. The results are summed up in the original paper (p. 298) in the sentence "Es

scheint also Identität vorzuliegen" (see also p. 292). In this respect, however, the results of Rowe and Davies were more definite, although again the proof depends on the comparison of the melting points of the two dinitro-naphthalic anhydrides, which melt above 310° with decomposition. However, these authors state that the products are identical.

e. Preparation of 4:5-Dinitro-1-naphthoic acid from the above mercuration product.

11 gms. mercuration product
25 c.c. 2 N sodium hydroxide
100 c.c. concentrated hydrochloric acid

The mercuration product was dissolved in the sodium hydroxide solution, and the chloromercuri-derivative precipitated as a dark brown solid by the addition of the concentrated hydrochloric acid.

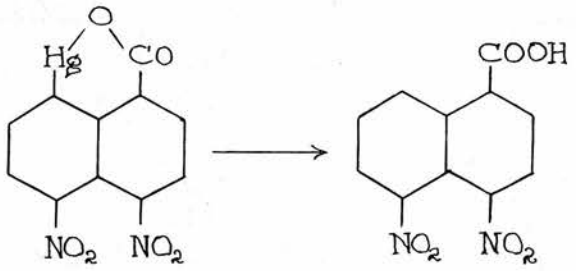
After boiling under reflux for 3 hours and allowing to stand overnight, the dark brown solid was filtered off, washed with water and dried at 100°.

The solid was dissolved in alcohol and boiled out several times with animal charcoal. After removing the alcohol by evaporation, the resulting solid was recrystallised twice from glacial acetic acid, when the product was obtained as a buff-coloured crystalline solid which, under the microscope, appeared as colourless needles.

Yield, 3·4 gms., representing 55% of the theoretical.

Melting point, 265°.

As in the previous case only one possible isomer can be formed, namely, 4:5-dinitro-1-naphthoic acid. This was confirmed by taking a mixed melting point with this acid and 4:5-dinitro-1-naphthoic acid, as prepared on p. 38 , no depression being observed.




This work was further confirmation of the structure assigned to dinitroacenaphthenequinone.

Ekstrand (J. pr. [2], 1888, 38, 256) prepared 4:5-dinitro-1-naphthoic acid by the nitration of α-naphthoic acid and also by the nitration of 5-nitro-1-naphthoic acid.

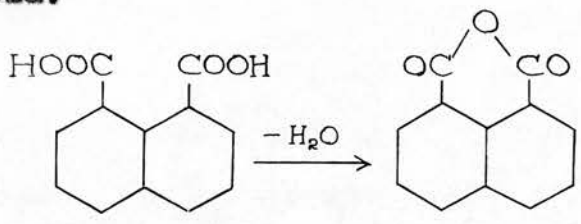
## III B. SYNTHESIS Of NITRO-BROMO-NAPHTHOIC ACIDS From NAPHTHALIC ANHYDRIDE. PREPARATION Of A NEW DINITRONAPHTHALENE.

### 1. Preparation of Naphthalic Anhydride.

Naphthalic acid, 10 gms., was placed in a 100 c.c. wide-necked flask. The flask was fitted with a cork which carried a very wide delivery tube and one end of a copper tube spiral, the lower end of which was just above the surface of the naphthalic acid.

A current of air, preheated by passing through the heated copper spiral, was passed over the naphthalic acid, and the flask was immersed as deeply as possible in an oil bath heated to 240-260°. By this means naphthalic anhydride sublimed over through the condenser as pale yellowish-white needles of melting point 270·5-271·5°.

Average yield, 6 gms., representing 66% of the theoretical. Some carbonisation occurred, diminishing the yield.




The naphthalic anhydride was used without

further purification.

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## 2. 3-Nitro-8-bromo-1-naphthoic Acid.

### a. Preparation of 3-nitro-naphthalic anhydride.

Ref. - Graebe and Briones, Ann., 1903, 327, 84.

12 gms. naphthalic anhydride

120 c.c. concentrated sulphuric acid

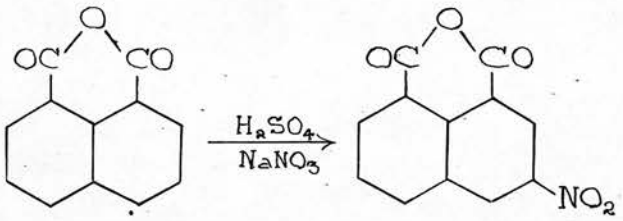
5·1 gms. powdered sodium nitrate.

The naphthalic anhydride was dissolved in the sulphuric acid, and the sodium nitrate (1 mole per mole of anhydride) slowly added, with constant shaking, to the cooled solution. A considerable amount of heat was developed.

After the addition was complete the flask was heated on a boiling water-bath for quarter-of-an-hour, allowed to cool and poured on ice, when a yellowish solid separated out. The mixture was allowed to stand overnight and the solid matter then filtered off, washed with cold water and dried at 100°.

It was recrystallised from glacial acetic acid from which the nitro-naphthalic anhydride was obtained as yellow crystals of melting point 247°.

Yield, 11·5 gms., representing 78% of the theoretical.

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b. Mercuration of 3-nitro-naphthalic anhydride.

Ref.- Leuck, Perkins and Whitmore, J.A.C.S., 1929, 51, 1831.

10 gms. 3-nitro-naphthalic anhydride

3·5 gms. sodium hydroxide

9 gms. yellow mercuric oxide.

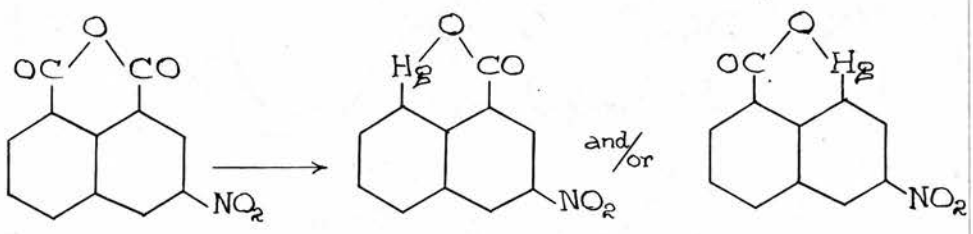
A solution of sodium 3-nitro-naphthalate was prepared by dissolving the nitro-naphthalic anhydride and sodium hydroxide together in 200 c.c. of water. The mercuric oxide was dissolved by heating with 30 c.c. water and 10 c.c. glacial acetic acid.

These two solutions were mixed together in a 500 c.c. pyrex bolt-head flask, and the whole made distinctly acid with acetic acid, when a yellow suspension formed. After refluxing for 100 hours, a test portion deposited no metallic mercury on a clean copper wire - the mercuration product, however, was not readily soluble in sodium hydroxide.

The solid was filtered off, washed with water, alcohol, and ether, and dried at 100°. It was a pale creamy-yellow powder.

Yield, 15·5 gms., representing 91% of the theoretical.

As in the case of the mercuration of 4-nitro-naphthalic acid (p. 122), either one or other of two isomers or a mixture of both is possible, depending on which of the two carboxyl groups is replaced by mercury.




3-Nitro-anhydro-8-hydroxy-mercuri-1-naphthoic Acid. 6-Nitro-isomer.

---

c. Bromination of the above mercuration product.

15 gms. mercuration product

6 gms. bromine

The mercuration product was suspended in 150 c.c. glacial acetic acid, and the bromine, which was dissolved in 40 c.c. of a concentrated solution of sodium bromide, was slowly added with stirring to the

cooled suspension over a period of 1 hour.

After the addition of the bromine solution, the mixture was heated to 90° for quarter-of-an-hour. The yellowish-brown solution thus obtained was poured into 300 c.c. water, with stirring, when a yellow solid separated out, which after standing overnight was filtered off, washed with water and dried at 100°.

It was a creamy-yellow solid, weight 9 gms., and melting at 200-225°.

Repeated recrystallisation from glacial acetic acid gave a product melting at 240-242°, the melting point being unaffected by further recrystallisation.

Yield, 3 gms.

In bulk, the substance was a pale pink-coloured crystalline solid, but under the microscope appeared as colourless plates. It was acidic and contained bromine (Beilstein's copper wire test) and nitrogen (sodium fusion).

Analysis: Nitrogen by Micro-Dumas Method.

Found, 4·9%.

Calculated for nitro-8-bromo-1-naphthoic acid, 4·7%.

Hence the compound obtained was a mononitro-8-bromo-1-naphthoic acid.

The acid was found to be soluble in alcohol and acetic acid, slightly soluble in boiling water, and sparingly soluble in benzene and ligroin.

As this product was prepared from 3-nitro-naphthalic anhydride, it will either be 3-nitro-8-bromo-1-naphthoic acid or 6-nitro-8-bromo-1-naphthoic acid. If the bromine be removed from the 8-position, either 3-nitro- or 6-nitro-1-naphthoic acid will be obtained (both of which are known) depending on the structure of the intermediate nitro-bromo-acid.

---

d. Dehalogenation of the above x-nitro-8-bromo-1-naphthoic acid.

0·5 gms. x-nitro-8-bromo-1-naphthoic acid

5 c.c. toluene

0·5 gms. copper bronze

The acid, toluene and copper were placed together in a small round-bottomed flask and boiled under reflux for 2 hours.

After some time the copper lost its bright appearance and a yellowish-brown deposit formed.

Aqueous sodium hydroxide was added and the contents of the flask warmed for a few minutes. The product was filtered into a separating funnel, the lower aqueous layer separated from the toluene and acidified with nitric acid. A dark brown precipitate formed, which was filtered off, washed with water and dried.

This solid was dissolved in boiling acetic acid and boiled out with animal charcoal. On cooling, crystals separated, which on further recrystallisation melted at 268-269°.

Yield, 0·2 gms.

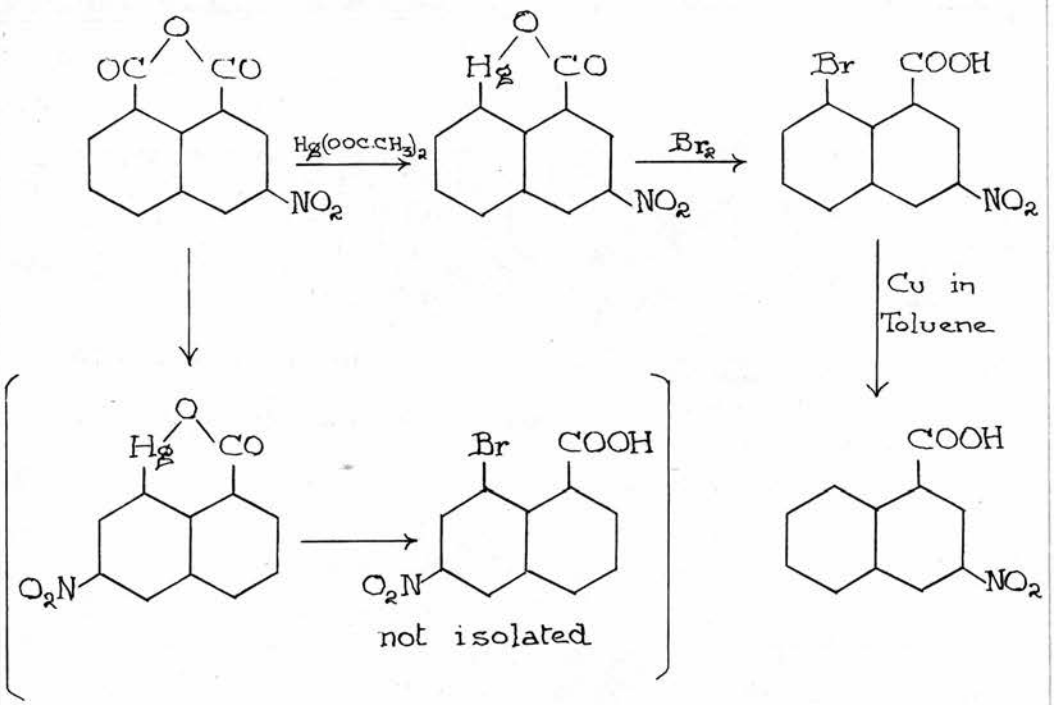
The compound was acidic and contained nitrogen but no halogen. It was a nitro-naphthoic acid and, as previously stated, must have been either 3-nitro- or 6-nitro-1-naphthoic acid. The melting point proved it to be the former. Leuck, Perkins and Whitmore (loc.cit.) quote 270·5-271·5° for the melting point of 3-nitro-1-naphthoic acid, and 227-227·5° for 6-nitro-1-naphthoic acid. A 55% yield was therefore obtained in the above dehalogenation.

The acid here obtained being 3-nitro-1-naphthoic acid proved that the acid from which it was derived was 3-nitro-8-bromo-1-naphthoic acid.

The reason for the comparatively small yield of 3-nitro-8-bromo-1-naphthoic acid is probably that a mixture of the 3-nitro and 6-nitro acids is produced, the latter in smaller bulk than the former, so that in the purification of the product only the 3-nitro acid is isolated, the 6-nitro-acid being lost.

This result is in agreement with the observations of Whitmore and his co-workers (loc. cit.). They obtained 6-nitro-1-naphthoic acid and 3-nitro-1-naphthoic acid by boiling the above mercuration product with

hydrochloric acid. A much larger yield of the 3-nitro acid than of the 6-nitro acid was obtained. The quantities of material used in the present experiments were very much smaller than those used by the above workers, making the isolation of the 6-nitro isomer more or less impossible.

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Preparation of Methyl 3-nitro-8-bromo-1-naphthoate.

0·5 gms. 3-nitro-8-bromo-1-naphthoic acid

5 c.c. purified thionyl chloride

15 c.c. dry methyl alcohol

The acid chloride was prepared by boiling the acid and thionyl chloride together under reflux in a small round-bottomed flask fitted with a ground-in reflux condenser, the flask being heated on a boiling

water-bath.

After about 1 hour, all gas evolution had ceased. The heating was continued for another hour but complete solution was not obtained, the acid chloride being apparently somewhat insoluble in thionyl chloride. Excess thionyl chloride was removed by distillation under reduced pressure.

To the semi-solid acid chloride the methyl alcohol was cautiously added, when a vigorous effervescence took place and hydrogen chloride gas was evolved. After the addition of the alcohol, the contents of the flask were boiled under reflux for 1 hour, and then the alcohol was removed by evaporation.

The ester was only sparingly soluble in benzene and ether, and so could not be extracted and purified in the usual way. It was therefore boiled up with sodium carbonate and filtered, the insoluble portion being washed with water, dried, and recrystallised from ligroin. In bulk, the ester was a very pale yellowish-white solid which appeared to be microcrystalline under the microscope.

Yield, 0·3 gms. Melting point 173°.

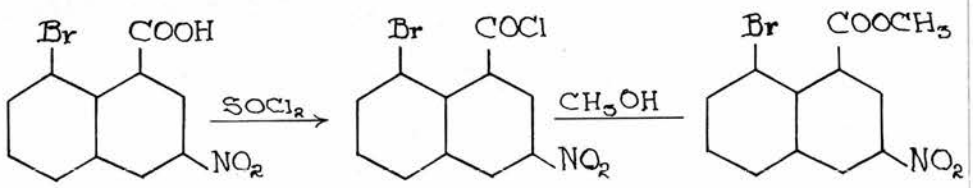
Unchanged acid (0·08 gms., m.p. 240-242°) was recovered by acidifying the sodium carbonate extract and recrystallising the precipitate from acetic acid.

Analysis. Nitrogen by Micro-Dumas Method.

| | |
|---|---|
| Found, | 4·6% |
| Calculated for methyl 3-nitro-8-bromo-1-naphthoate, | 4·5% |

The yield quoted above, allowing for recovered acid, is 68% of the theoretical.

The ester is soluble in alcohol and acetic acid, but less so in ligroin, benzene and ether.

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Preparation of ethyl 3-nitro-8-bromo-1-naphthoate.

0·5 gms. 3-nitro-8-bromo-1-naphthoic acid

5 c.c. purified thionyl chloride

15 c.c. dry ethyl alcohol

The acid chloride was formed as above, and the ethyl ester prepared from it by the addition of the ethyl alcohol, the remainder of the preparation being carried out in the same way as for the methyl ester.

The ester was obtained as pale yellowish-white micro-crystals from ligroin.

Yield, 0·3 gms., representing 69% of the theoretical, allowing for 0·1 gm. recovered acid.

Melting point of ester, 155-156°.

Analysis. Nitrogen by Micro-Dumas Method.

| | |
|---|---|
| Found, | 4·4% |
| Calculated for ethyl 3-nitro-8-bromo-1-naphthoate, | 4·3% |

The ester is soluble in alcohol and acetic acid, but less soluble in ligroin, benzene and ether.

---

## 3. 3:6-Dinitro-8-bromo-1-naphthoic Acid and 2:7-Dinitronaphthalene.

Francesconi and Bargellini (Gazz. Chim. Ital., 1902, 32, 94) record the preparation of a dinitro-naphthalic acid from naphthalic anhydride by direct nitration. This acid has been used as starting material in the following series of preparations. These authors did not determine the positions of the nitro-groups. Naphthalic anhydride, however, on mono-nitration, yields the 3-nitro isomer, and hence the dinitro-compound will have one nitro group in the 3-position. The position of the second nitro group will meanwhile be designated by x.

a. Preparation of 3:x-Dinitro-naphthalic acid.

Ref. - Francesconi and Bargellini, loc. cit.

15 gms. naphthalic anhydride
300 gms. concentrated sulphuric acid
250 gms. fuming nitric acid

The naphthalic anhydride was carefully dissolved, with cooling, in the concentrated sulphuric acid. A bluish fluorescent solution was obtained.

To this solution the fuming nitric acid was added, and after standing for 2 hours at room temperature, with occasional shaking, the mixture was poured into cold water. A yellowish-white solid separated out, leaving the mother liquor yellow in colour.

The product was filtered off, washed with cold water, and recrystallised several times from boiling water from which the dinitro-naphthalic acid was obtained as silver-white plates.

Yield, 14·5 gms., representing 63% of the theoretical.

Melting point, 208-210°.

---

b. Mercuration of 3:x-dinitro-naphthalic acid.

10 gms. 3:x-dinitro-naphthalic acid
3 gms. sodium hydroxide
7·6 gms. yellow mercuric oxide

The mercuration was carried out as in previous

cases. A solution of sodium 3:x-dinitro-naphthalate was prepared by dissolving the acid in a solution of the sodium hydroxide in 200 c.c. water. To this was added a solution of mercuric acetate prepared by dissolving the mercuric oxide in 30 c.c. water and 10 c.c. glacial acetic acid.

Sufficient glacial acetic acid was added to make the mixture distinctly acid, a yellowish-white suspension being formed. On boiling under reflux for 100 hours, the suspension became dark brown in colour, the boiling being accompanied by violent "bumping". At the end of that time a test portion deposited no metallic mercury on a clean copper wire.

The product was filtered while hot, the dark brown solid being washed with water, alcohol and ether, and dried at 100°.

Weight, 12·5 gms.

On cooling, the filtrate deposited a crop of brownish-coloured crystals which after repeated recrystallisation from boiling water proved to be unchanged 3:x-dinitro-naphthalic acid.

Weight, 1·5 gms. Melting point 208-210°.

The percentage yield of mercuration product, allowing for recovered acid, is therefore 92% of the theoretical.

---

c. Bromination of the above mercuration product.

12 gms. mercuration product

4·5 gms. bromine

The bromine, dissolved in 40 c.c. of a concentrated solution of sodium bromide, was added slowly over a period of one hour to a cooled suspension of the mercuration product in 150 c.c. glacial acetic acid, with efficient mechanical stirring.

When the addition was complete the mixture was heated to 90° for quarter-of-an-hour, a brown solution being obtained which was poured into 300 c.c. cold water, with stirring. A pink-coloured solid separated out. After standing overnight the precipitate was filtered off, washed with cold water and dried.

Weight, 5 gms.

The product was boiled out twice with animal charcoal in glacial acetic acid, and recrystallised twice from glacial acetic acid. It was obtained as a pink-coloured crystalline solid which appeared as colourless plates under the microscope. Qualitative analysis proved it to be acidic and to contain bromine and nitrogen.

Yield, 2·5 gms. Melting point, 273-275°, unchanged by further recrystallisation.

Analysis. Nitrogen by Micro-Dumas Method.

Found, 8·3 %

Calculated for x:x'-dinitro-8-bromo-1- naphthoic acid, 8·2 %

The compound was therefore x:x'-dinitro-8-bromo-1-naphthoic acid. It is soluble in alcohol and acetic acid in the cold, soluble in hot benzene, but only slightly soluble in ether. It was observed that this acid has a very bitter taste.

The yield quoted above represents 28% of the theoretical.

---

Preparation of methyl x:x'-dinitro-8-bromo-1-naphthoate.

0·5 gms. x:x'-dinitro-8-bromo-1-naphthoic acid

5 c.c. purified thionyl chloride

15 c.c. dry methyl alcohol

The acid chloride was prepared by boiling the acid and thionyl chloride together under reflux on a boiling water-bath for 1 hour, when all gas evolution had ceased.

After removing the excess thionyl chloride by distillation under reduced pressure, the methyl alcohol was carefully added to the dark-coloured oily acid chloride, hydrogen chloride gas being evolved with effervescence. When all the methyl alcohol was added, the product was boiled under reflux for 1 hour.

The alcohol was removed by evaporation and the semi-solid ester taken up in benzene, the solution being tinged red. Unchanged acid was removed by

washing the solution with sodium carbonate and water. After drying over calcium chloride, the solvent was removed by evaporation, leaving a reddish-yellow syrup. This syrup was dissolved in boiling absolute alcohol, from which, on cooling, the ester separated as pink-coloured crystals, which under the microscope appeared as colourless truncated rectangular prisms.

Yield, 0·34 gms., representing a 66% yield.

Melting point, 137-138°.

Analysis. Nitrogen by Micro-Dumas Method.

| | |
|---|---|
| Found, | 8·1% |
| Calculated for methyl x:x'-dinitro-8-bromo-1-naphthoate, | 7·9% |

The ester is soluble in cold benzene and chloroform, and in hot alcohol and acetic acid, but is only sparingly soluble in ether.

---

Preparation of ethyl x:x'-dinitro-8-bromo-1-naphthoate.

0·5 gm. x:x'-dinitro-8-bromo-1-naphthoic acid

5 c.c. purified thionyl chloride

15 c.c. dry ethyl alcohol

The ethyl ester, which was prepared in the same way as the methyl ester, was recrystallised from boiling alcohol from which, on cooling, it separated

as pink-coloured crystals. These crystals were similar to those of the methyl ester, appearing under the microscope as colourless truncated rectangular prisms. In solubility the ethyl and methyl esters were also similar.

Yield, 0·36 gm. representing a 67% yield.

Melting point, 205-207°.

Analysis. Nitrogen by Micro-Dumas Method.

| | |
|---|---|
| Found, | 7·6% |
| Calculated for ethyl x:x'-dinitro-8-bromo-1-naphthoate, | 7·6% |

---

d. Preparation of x:x'-dinitro-1-naphthoic acid.

12 gms. mercuration product

50 c.c. 2 N. sodium hydroxide

120 c.c. concentrated hydrochloric acid

The mercuration product and sodium hydroxide were warmed together; only part of the solid dissolved, giving a dark brown solution.

On the addition of the hydrochloric acid the contents of the flask became much lighter in colour.

After boiling under reflux for 4 hours the product was allowed to stand overnight and then filtered, the dark brown solid obtained being washed with water and dried at 100°. It was dissolved in

boiling absolute alcohol and boiled out twice with animal charcoal. The alcohol was removed by evaporation, and the remaining solid recrystallised twice from glacial acetic acid. A buff-coloured crystalline solid was obtained, which appeared as colourless needles when viewed under the microscope.

Yield, 4·0 gms. Melting point, 273·5-274°.

Analysis. Nitrogen by Micro-Dumas Method.

| | |
|---|---|
| Found, | 10·6% |
| Calculated for x:x'-dinitro-1-naphthoic acid, | 10·7% |

The product was therefore x:x'-dinitro-1-naphthoic acid, so the above yield represents 59% of the theoretical. It is soluble in alcohol, and less soluble in acetic acid and benzene, but only sparingly soluble in ether.

---

Preparation of methyl x:x'-dinitro-1-naphthoate.

0·5 gms. x:x'-dinitro-1-naphthoic acid
5 c.c. purified thionyl chloride
10 c.c. dry methyl alcohol

The ester was prepared by the same method as used for previous esterifications (p.145).

After the removal of the alcohol, it was found that the ester was only sparingly soluble in cold

benzene or ether, so the solid product was boiled out with sodium carbonate solution to remove unchanged acid, and filtered. The insoluble portion was washed with water and dried. Recrystallisation from absolute alcohol gave the ester as colourless needles aggregated in fan-shaped clusters, or from benzene as colourless prisms. In bulk, the ester was a pale yellowish-white powder.

Yield, 0·3 gm., representing 57% of the theoretical.

Melting point, 196-197°.

Analysis. Nitrogen by Micro-Dumas Method.

Found, 10·0%

Calculated for methyl x:x'-dinitro-1-naphthoate, 10·15%

---

Preparation of ethyl x:x'-dinitro-1-naphthoate.

0·5 gm. x:x'-dinitro-1-naphthoic acid

5 c.c. purified thionyl chloride

10 c.c. dry ethyl alcohol

The ethyl ester was prepared in the same way as the methyl ester.

When recrystallised from absolute alcohol, the ester was obtained as a pale yellowish-white powder which appeared under the microscope as colourless

needles aggregated in fan-shaped clusters. From benzene it separated as colourless prisms.

Yield, 0·3 gm., representing a 54% yield.

Melting point, 145-146°.

Analysis. Nitrogen by Micro-Dumas Method.

Found, 9·6%

Calculated for ethyl x:x'-dinitro-1-naphthoate, 9·7%

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Several nitro compounds have thus been prepared from dinitro-naphthalic anhydride. The constitutions of these compounds are dependent upon the structure of the dinitro-naphthalic acid which, however, has not yet been determined.

These related compounds are x:x'-dinitro-8-bromo-1-naphthoic acid, x:x'-dinitro-1-naphthoic acid, and their methyl and ethyl esters.

In the literature no dinitro-8-bromo-1-naphthoic acids are recorded, but three dinitro-1-naphthoic acids are listed, namely, 4:5-dinitro-1-naphthoic acid (m.p., 265°), 5:8-dinitro-1-naphthoic acid (m.p., 218°), and 5:β-dinitro-1-naphthoic acid (m.p., 215°). Apart from any theoretical considerations, the melting point of the above x:x'-dinitro-1-naphthoic acid (273·5-274°) proves that it is not one of these.

As naphthalic anhydride mono-nitrates in the 3-position, it is probabld that it dinitrates in the

3:6-positions. The following experimental work was carried out to settle this point.

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e. Determination of the positions of the nitro-groups in 3:x-dinitro-naphthalic acid, and in the related compounds prepared above.

It was purposed using the "copper quinoline" method for the decarboxylation of 3:x-dinitro-naphthalic acid, but as this method had never been used for the removal of two carboxyl groups simultaneously, a preliminary experiment was carried out with naphthalic acid. It was found that naphthalene was readily obtainable from naphthalic acid by this means, and the reaction was therefore applied to 3:x-dinitro-naphthalic acid as described below.

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(i) Decarboxylation of 3:x-dinitro-naphthalic acid.

2 gms. 3:x-dinitro-naphthalic acid
5 c.c. dry quinoline
2 gms. copper bronze

The acid was dissolved in the boiling quinoline, as in previous decarboxylations, and the copper bronze carefully added in small portions. Vigorous frothing

accompanied the addition of the copper, and the product became dark in colour.

After boiling for 15 minutes, the cooled product was extracted with a large volume of ether, and the filtered extract washed successively with dilute hydrochloric acid, aqueous sodium carbonate, and water. The solution was dried over calcium chloride, and the ether removed by evaporation, the resulting yellow-coloured solid being recrystallised from acetic anhydride.

A yellow crystalline solid was obtained, which under the microscope appeared as broad colourless needles.

Yield, 0·4 gm. Melting point, 234°, unchanged by further recrystallisation.

The product was non-acidic, but contained nitrogen.

Analysis. Nitrogen by Micro-Dumas Method.

| | |
|---|---|
| Found, | 12·8%. |
| Calculated for 2:x-dinitronaphthalene, | 12·8% |

The compound obtained was therefore a dinitronaphthalene, so that the yield quoted above represents 27% of the theoretical. It was observed that this dinitronaphthalene dissolves readily in acetic acid and benzene, is less soluble in alcohol, and only sparingly soluble in ether.

Disregarding any theoretical considerations, and in view of the known structure of the mononitronaphthalic acid, the possible positions for the nitro-groups in the dinitronaphthalene are 1:2, 1:7, 2:6, 2:7, or 2:3. Of these, the melting point eliminates the first three, leaving the unknown 2:7-and 2:3-derivatives. The diaminonaphthalenes corresponding to the 2:3, 2:6-, and 2:7-structures are, however, all known, so that the reduction of the above dinitronaphthalene should prove the positions of the nitro groups. In any case, it is extremely unlikely that the two nitro-groups would occupy adjacent (2:3) positions, leaving the 2:7-structure as the most probable.

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(ii) Reduction of the above 2:x-dinitronaphthalene.

0·25 gm. 2:x-dinitronaphthalene
100 c.c. absolute alcohol
2 gms. tin

The dinitronaphthalene was dissolved in the alcohol, the solution being boiled under reflux. After the addition of the tin, concentrated hydrochloric acid was added in successive small quantities (2 c.c. at a time) to the boiling solution until all

the tin was dissolved - about 2 hours time.

A black residue which remained was removed by filtration. To the cold filtrate sodium hydroxide was added until the stannic hydroxide which precipitated was redissolved.

The base was extracted with ether, the extract evaporated to dryness, and the resulting dark brown solid recrystallised twice from boiling water. A white solid was obtained, which appeared as colourless plates when viewed under the microscope.

Yield, 0·1 gm., representing 55% of the theoretical.

Melting point, 159°.

This melting point corresponds with that of 2:7-diaminonaphthalene and thus eliminates the 2:3- (m.p. 191°) and the 2:6- (m.p. 216-218°) compounds. The base obtained is therefore 2:7-diamino-naphthalene, which in this way becomes for the first time a comparatively readily accessible compound.

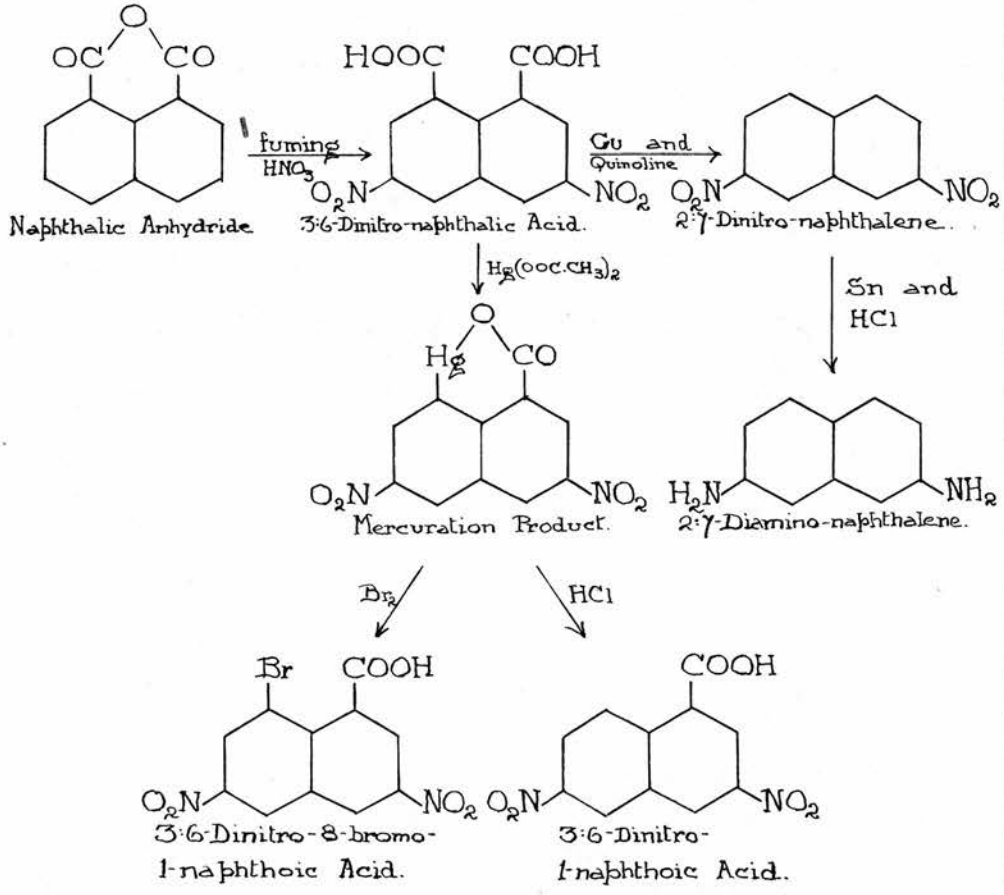
Previously it had been prepared from 2:7-dihydroxynaphthalene by treating with ammonia at 260-270° (Bamberger and Schieffelin, Ber., 1889, 22, 1384) which in turn was obtained from naphthalene-2:7-disulphonic acid by heating with potassium hydroxide.

Since the base is 2:7-diaminonaphthalene, the dinitro-derivative from which it was obtained must be

2:7-dinitronaphthalene, which is a new compound.

Tracing this conclusion back, the dinitro-naphthalic acid from which the dinitronaphthalene was obtained must be 3:6-dinitronaphthalic acid. Further, the dinitro-bromo-naphthoic acid, prepared as on p.144, must be 3:6-dinitro-8-bromo-1-naphthoic acid, and the dinitro-naphthoic acid, prepared as on p.147, must be 3:6-dinitro-1-naphthoic acid.

These relationships are more readily followed when represented schematically.



## S U M M A R Y.

1. 8-Bromo-1-naphthoic acid, which nitrates in the 5-position, has been further nitrated. The resulting dinitro-bromo acid was dehalogenated by boiling with copper bronze in toluene, and the product decarboxylated by boiling with copper bronze in quinoline to yield 1:8-dinitronaphthalene, thus proving the dinitro-bromo acid to be 4:5-dinitro-8-bromo-1-naphthoic acid.

On bromination, 8-bromo-1-naphthoic acid yielded a dibromo acid which proved to be 5:8-dibromo-1-naphthoic acid, since from it on partial dehalogenation 5-bromo-1-naphthoic acid was obtained.

Attempts to brominate 5:8-dibromo-1-naphthoic acid failed to produce a tribromo acid, decarboxylation taking place with the production of a mixture of higher bromo-naphthalenes.

2. The preparation of 8-hydroxy-1-naphthoic acid from 8-bromo-1-naphthoic acid by boiling with sodium hydroxide in presence of copper bronze has been studied and the most favourable conditions for the

reaction determined.

Although the hydroxy acid could not be converted into naphtholactone simply by heating it, the conversion was effected by boiling in benzene solution with phosphorus pentoxide.

Three methods for determining the orientation of substituted 8-hydroxy acids were investigated. The first which consisted in treating the hydroxy-acid with phosphorus pentabromide in an endeavour to convert the hydroxy-acid to the corresponding bromo-acid produced only 5-bromonaphtholactone, and so was of no value. The second, an attempt to decarboxylate the hydroxy-acid to yield the corresponding naphthol, likewise failed, naphtholactone being the final product. However, the third method appears as if it would be applicable to the problem although no substituted hydroxy acids were available at the time. This method involved the methylation of the substituted hydroxy acid and the decarboxylation of the resulting methoxy acid. That such methoxy acids could be successfully decarboxylated was shown by the conversion of 5-nitro-8-methoxy-1-naphthoic acid (prepared from 5-nitro-8-bromo-1-naphthoic acid and sodium methoxide) into 4-nitro-1-methoxynaphthalene.

Owing to the lability of the bromine atom in 8-bromo-1-naphthoic acid, it was thought that this acid might be converted into naphthastyril. After several

unsuccessful attempts, it was found that the reaction could be simply accomplished by heating the bromo-acid under pressure in solution in ammonium hydroxide in presence of a catalyst, the yield being 82% of the theoretical.

By a modification of Ekstrand's method naphthastyril was dibrominated in 90% yield, the bromine atoms in the product being shown to occupy the 5 and 7 positions by diazotisation, followed by decarboxylation of the resulting dibromo-naphthoic acid. The final product was identified as 1:3-dibromonaphthalene. Accordingly, Ekstrand's dichloro- and dinitro-naphthastyrils must also have their substituent groups in the 5 and 7 positions, since the former was prepared in like manner to the dibromo-derivative, and the latter from the dibromo-compound by treatment with nitric acid.

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3. The mono- and dinitro-derivatives of acenaphthene-quinone on oxidation to the corresponding naphthalic acids, followed by mercuration and bromination, have given rise to 4-nitro-8-bromo-1-naphthoic acid and 4:5-dinitro-8-bromo-1-naphthoic acid respectively. The identity of the former was proved by the fact that on admixture with 5-nitro-8-bromo-1-naphthoic acid a depression of the melting point was observed,

the 5- and the 4-nitro acids being the only two possibilities. A mixed melting point with 4:5-dinitro-8-bromo-1-naphthoic acid, prepared by direct nitration of 8-bromo-1-naphthoic acid, proved the constitution of the dinitro-bromo-acid. This confirmed the results of the workers who first dinitrated acenaphthenequinone and formulated the product as 5:6-dinitroacenaphthenequinone, basing their proof on the melting points of the corresponding naphthalic anhydrides. By acid hydrolysis of the mercuration product from the dinitro-acenaphthenequinone, 4:5-dinitro-1-naphthoic acid was obtained, which proved to be identical with the acid prepared by dehalogenation of 4:5-dinitro-8-bromo-1-naphthoic acid, and also with the dinitro acid isolated by Ekstrand from the nitration products of α-naphthoic acid.

Naphthalic anhydride, on nitration, yielded a mononitro-derivative, which, on mercuration and bromination, gave rise to 3-nitro-8-bromo-1-naphthoic acid. The orientation of this acid was determined by dehalogenation to form 3-nitro-1-naphthoic acid.

On dinitration, naphthalic anhydride gave a dinitro-naphthalic acid, from which by the removal of the carboxyl groups ("copper and quinoline" method) a dinitronaphthalene was obtained. This dinitro-naphthalene was proved to be the hitherto unknown

2:7-derivative by reducing it to the known 2:7-diaminonaphthalene. Accordingly, the dinitro-naphthalic acid was the 3:6-derivative. From this acid, by mercuration, a product was obtained which on hydrolysis gave 3:6-dinitro-1-naphthoic acid, and on bromination formed 3:6-dinitro-8-bromo-1-naphthoic acid, both of which are new compounds.

Where possible, the methyl and ethyl esters of all new acids were prepared.

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